Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

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Final Report, October 2006

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ABSTRACT

This final report presents and discusses results from a mercury control process development project entitled "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems." The objective of this project was to demonstrate at pilot scale a mercury control technology that uses solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. Oxidized mercury is removed in downstream wet flue gas desulfurization (FGD) absorbers and leaves with the FGD byproducts. The goal of the project was to achieve 90% oxidation of elemental mercury in the flue gas and 90% overall mercury capture with the downstream wet FGD system.

The project was co-funded by EPRI and the U.S. Department of Energy's National Energy Technology Laboratory (DOE NETL) under Cooperative Agreement DE-FC26-01NT41185. Great River Energy (GRE) and City Public Service (now CPS Energy) of San Antonio were also project co-funders and provided host sites. URS Group, Inc. was the prime contractor. Longer-term pilot-scale tests were conducted at two sites to provide catalyst life data. GRE provided the first site, at their Coal Creek Station (CCS), which fires North Dakota lignite, and CPS Energy provided the second site, at their Spruce Plant, which fires Powder River Basin (PRB) coal.

Mercury oxidation catalyst testing began at CCS in October 2002 and continued through the end of June 2004, representing nearly 21 months of catalyst operation. An important finding was that, even though the mercury oxidation catalyst pilot unit was installed downstream of a high-efficiency ESP, fly ash buildup began to plug flue gas flow through the horizontal catalyst cells. Sonic horns were installed in each catalyst compartment and appeared to limit fly ash buildup.

A palladium-based catalyst showed initial elemental mercury oxidation percentages of 95% across the catalyst, declining to 67% after 21 months in service. A carbon-based catalyst began with almost 98% elemental mercury oxidation across the catalyst, but declined to 79% oxidation after nearly 13 months in service. The other two catalysts, an SCR-type catalyst (titanium/ vanadium) and an experimental fly-ash-based catalyst, were significantly less active.

The palladium-based and SCR-type catalysts were effectively regenerated at the end of the long-term test by flowing heated air through the catalyst overnight. The carbon-based catalyst was not observed to regenerate, and no regeneration tests were conducted on the fourth, fly-ash-based catalyst.

Preliminary process economics were developed for the palladium and carbon-based catalysts for a scrubbed, North Dakota lignite application. As described above, the pilot-scale results showed the catalysts could not sustain 90% or greater oxidation of elemental mercury in the flue gas for a period of two years. Consequently, the economics were based on performance criteria in a later

DOE NETL solicitation, which required candidate mercury control technologies to achieve at least a 55% increase in mercury capture for plants that fire lignite. These economics show that if the catalysts must be replaced every two years, the catalytic oxidation process can be 30 to 40% less costly than conventional (not chemically treated) activated carbon injection if the plant currently sells their fly ash and would lose those sales with carbon injection. If the plant does not sell their fly ash, activated carbon injection was estimated to be slightly less costly. There was little difference in the estimated cost for palladium versus the carbon-based catalysts.

If the palladium-based catalyst can be regenerated to double its life to four years, catalytic oxidation process economics are greatly improved. With regeneration, the catalytic oxidation process shows over a 50% reduction in mercury control cost compared to conventional activated carbon injection for a case where the plant sells its fly ash.

At Spruce Plant, mercury oxidation catalyst testing began in September 2003 and continued through the end of April 2005, interrupted only by a host unit outage in late February/early March 2005. With a baghouse upstream of the catalysts, sonic horns did not appear to be necessary and were never installed. Pressure drop across the four catalysts remained low.

Catalyst activity for elemental mercury oxidation was difficult to evaluate at this site. It was found that the baghouse effectively oxidized elemental mercury in the flue gas, with the baghouse outlet flue gas averaging 81% mercury oxidation. This oxidation resulted in little elemental mercury remaining in the flue gas going to the oxidation catalyst pilot unit. In many instances, catalyst outlet elemental mercury concentrations were near detection limits for the measurement methods employed, so mercury oxidation percentages across the catalyst were uncertain.

More sensitive mercury semi-continuous emissions monitors (SCEMs) were used to evaluate catalyst performance in the latter half of the test period, with more consistent results. These results showed that, through the end of the test period, two catalyst types (palladium and gold) were more active for elemental mercury oxidation than the other two, an experimental carbon-based catalyst and an SCR-type catalyst. The palladium catalyst achieved greater than 90% elemental mercury oxidation across the catalyst after 8 months of service and 51% oxidation after 18 months. This represents more rapid activity loss than was measured for the palladium catalyst at CCS, though. The gold catalyst results were similar to the palladium results, showing greater than 90% elemental mercury oxidation across the catalyst after 8 months and 47% oxidation after 18 months.

At the end of the long-term test, all four catalysts were observed to regenerate in activity after treatment with heated air overnight. Regeneration conditions were similar to those used at CCS.

Cost estimates were developed for applying oxidation catalyst technology to a power plant that fires PRB coal and has a baghouse for particulate control followed by a wet FGD system. The oxidation catalyst cost was estimated for achieving a minimum of 75% oxidation of the elemental mercury in the baghouse outlet flue gas, which corresponds with at least 90% overall mercury oxidation in the flue gas going to the wet FGD system and 82% overall mercury capture. These costs were compared to estimates for an activated carbon injection system for

upstream of the baghouse, designed to achieve 82% overall mercury capture (including capture of remaining mercury by the downstream FGD system).

In this comparison, the cost of oxidation catalyst technology was estimated to be significantly greater than the costs for an activated carbon injection system with similar overall mercury capture performance. However, it was determined that a plant configuration with a baghouse rather than an ESP for particulate control was particularly advantageous for the activated carbon injection process and disadvantageous for mercury oxidation catalysts. It is expected that a cost comparison for a PRB-fired plant with an ESP would be much more favorable for oxidation catalyst technology.

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CONTENTS

1 INTRODUCTION 1-1

Process Overview 1-2

Report Organization 1-3

2 EXECUTIVE SUMMARY 2-1

3 EXPERIMENTAL 3-1

Project Overview 3-1

Project Host Sites 3-3

Hg SCEM 3-3

Oxidation Catalyst Pilot Unit Description 3-5

4 RESULTS AND DISCUSSION 4-1

Laboratory Results 4-1

CCS Simulations 4-1

Spruce Simulations 4-11

Catalyst Supply 4-15

Pilot Test Program Results 4-20

CCS Results 4-20

Initial Pilot Unit Operation 4-20

CCS Long-term Catalyst Pressure-drop Results 4-27

CCS Catalyst Activity Results 4-33

CCS Catalyst Regeneration Test Results 4-41
CCS Flue Gas Characterization Results 4-43
Ontario Hydro Results – October 2002 4-44
Ontario Hydro Results – July 2003 4-45
Ontario Hydro Results – June 2004 4-48
Flue Gas Metals (Method 29) 4-50
Flue Gas Halogen Species (Method 26a) 4-52
Flue Gas Sulfuric Acid Concentrations (Controlled Condensation Method) 4-52
Flue Gas NO_2 Concentration 4-54
Spruce Pilot Test Program Results 4-55
Spruce Catalyst Pressure-drop Results 4-59
Spruce Catalyst Activity Results 4-60
Spruce Catalyst Regeneration Test Results 4-70
Spruce Flue Gas Characterization Results 4-75
Ontario Hydro Results – December 2003 4-75
Ontario Hydro Results – October 2004 4-80
Flue Gas Metals (Method 29) 4-84
Flue Gas Halogen Species (Method 26a) 4-86
Flue Gas Sulfuric Acid Concentrations (Controlled Condensation Method) 4-87
Other Flue Gas Characterization Results 4-87
Oxidation Catalyst Process Economics 4-89
Estimated Economics for a North Dakota Lignite/ESP Configuration 4-89
Assumptions 4-90
Base Case Economics for ND Lignite 4-93
Sensitivity Case Economics for ND Lignite at 55% Mercury Removal 4-94
Sensitivity Case Economics for ND Lignite at 90% Mercury Oxidation 4-97
Estimated Economics for a PRB-fired Plant with a Baghouse 4-99
Assumptions 4-99
Mercury Control Targets 4-102
Performance Estimates for Oxidation Catalysts and for Conventional Activated Carbon Injection 4-104
Base Case Economics 4-105
Sensitivity Case Economics 4-106

5 CONCLUSIONS 5-1

CCS Results 5-1

Spruce Results 5-3

6 REFERENCES 6-1

LIST OF FIGURES

Figure 1-1 General Process Flow Diagram for the Mercury Catalytic Oxidation Process.....1-2

Figure 3-1 Simplified P&ID for the Catalyst Pilot Unit (one of four catalyst chambers shown).....3-2

Figure 3-2 Schematic of EPRI Semi-continuous Mercury Analyzer.....3-4

Figure 3-3 Plan View of Final Catalyst Pilot Unit Design 3-6

Figure 3-4 Photograph of the Pilot Skid from the Side on the Inlet End, Near the Completion of its Mechanical Fabrication.....3-8

Figure 3-5 Photograph of the Pilot Skid from the Exit End, Near the Completion of its Mechanical Fabrication 3-9

Figure 3-6 Photograph of Pilot Unit Control Panel Prior to Installation on Pilot Skid 3-10

Figure 3-7 Pilot Skid as Installed at CCS.....3-11

Figure 3-8 Pilot Skid as Installed at Spruce Plant.....3-12

Figure 4-1 Elemental Mercury Oxidation Percentage vs. Area Velocity for SCR, C #6, and SBA #5 Catalyst Samples 4-4

Figure 4-2 Elemental Mercury Oxidation Percentage vs. Area Velocity for Pd #1 Catalyst Samples (all measurements made using Tris impingers) 4-6

Figure 4-3 Elemental Mercury Oxidation Percentage vs. Area Velocity for Pd #1 Catalyst Samples (all measurements, including those made using Tris and KCl impingers).....4-8

Figure 4-4 Effect of Area Velocity on Catalytic Oxidation of Hg^0 at Simulated Site 2 Conditions 4-14

Figure 4-5 Argillon Catalyst Block Ready for Installation in Pilot Unit.....4-15

Figure 4-6 Sample Catalyst Block for SBA #5, as Prepared by Catalyst Manufacturer.....4-16

Figure 4-7 Photograph of One of Three SBA #5 Catalyst Cans 4-17

Figure 4-8 Close-up of One of Three SBA #5 Catalyst Cans 4-18

Figure 4-9 Predicted vs. Actual Elemental Mercury Oxidation across Catalysts at CCS, October 2002 4-22

Figure 4-10 Apparent Loss of Activity versus Time in Service at CCS at 1500 acfm (2550 m^3/hr) Flue Gas Flow Rate.....4-23

Figure 4-11 Catalyst Chamber Pressure Drop versus Time in Service 4-24

Figure 4-12 Photograph Depicting Fly Ash Buildup on the Pd #1 Catalyst Surface in January 2003 4-25

Figure 4-13 Photograph Depicting the Surface of the Pd #1 Catalyst after Clean-up in January 2003 4-26

Figure 4-14 Pressure-drop Data for the Three Catalysts in Service at CCS through May 27 4-28

Figure 4-15 Typical Sonic Horn Installation on the Pilot Unit at CCS 4-31
Figure 4-16 Pressure-Drop Data for the Catalysts in Service at CCS, June through early January 2003 Note: 1 in. H_2O = 0.25 kPa. 4-31
Figure 4-17 Pressure-drop Data for the Catalysts in Service at CCS through June 2004 4-32
Figure 4-18 Activity for Hg^0 Oxidation versus Time for Pd #1 and C #6 Catalysts at CCS. 4-40
Figure 4-19 Activity for Hg^0 Oxidation versus Time for SCR and SBA #5 Catalysts at CCS 4-40
Figure 4-20 Close-up of One Catalyst Module after One Month of Operation at Spruce Plant 4-58
Figure 4-21 Photograph of a Catalyst Chamber at Spruce Showing Minimal Fly Ash Buildup after One Month of Operation 4-58
Figure 4-22 Pressure-Drop Data for the Catalysts in Service at Spruce through December Note: 1 in. H_2O = 0.25 kPa. 4-59
Figure 4-23 Spruce Catalyst Activity Data versus Time in Service 4-70
Figure 4-24 Trend Plot for Regeneration of the Pd #1 Catalyst 4-72
Figure 4-25 Trend Plot for Regeneration of the C #6 Catalyst 4-72
Figure 4-26 Trend Plot for Regeneration of the Gold Catalyst 4-73
Figure 4-27 Trend Plot for Regeneration of the SCR Catalyst 4-73

LIST OF TABLES

Table 3-1 Summary of Pilot Unit Instrumentation 3-7

Table 4-1 Catalyst Materials Considered for Evaluation in Pilot-scale Mercury Oxidation Tests at CCS 4-1

Table 4-2 Synthetic Flue Gas Conditions for CCS Simulations 4-2

Table 4-3 Laboratory Simulation Results for SCR, C #6, and SBA #5 Catalysts at CCS Conditions 4-3

Table 4-4 Laboratory Simulation Results for Pd #1 Catalyst Samples at CCS Conditions (all using Tris impingers) 4-5

Table 4-5 Laboratory Simulation Results for Pd #1 Catalyst Samples at CCS Conditions (all tests with KCl instead of Tris impingers when measuring elemental mercury concentrations) 4-7

Table 4-6 Honeycomb Dimensions and Actual vs. Predicted Catalyst Performance 4-8

Table 4-7 Catalyst Dimensions for the Laboratory Testing and Selected for the CCS Pilot Unit 4-11

Table 4-8 Catalyst Materials Considered for Evaluation in Pilot-scale Mercury Oxidation Tests 4-12

Table 4-9 Comparison of Laboratory Simulation Gas Conditions for the Two Host Sites 4-12

Table 4-10 Spruce Laboratory Simulation Results (average results using KCl and Tris impingers for measuring elemental mercury concentrations) 4-13

Table 4-11 Catalyst Dimensions for Oxidation Catalyst Pilot Unit at Spruce Plant 4-19

Table 4-12 October 2002 Catalyst Activity Results (Hg concentrations reported as measured, uncorrected for sample gas O_2 content) 4-21

Table 4-13 December 2002 Catalyst Activity Results (Hg concentrations reported as measured, uncorrected for sample gas O_2 content) 4-21

Table 4-14 Summary of the First Six Months of Hg^0 Oxidation Catalyst Activity Results at CCS 4-27

Table 4-15 Summary of Catalyst Activity Results from CCS, April 2003 (Hg concentrations reported as measured, uncorrected for sample gas O_2 content) 4-29

Table 4-16 Summary of Catalyst Activity Results from CCS, June 2003 (Hg concentrations reported as measured, uncorrected for sample gas O_2 content) 4-34

Table 4-17 Oxidation Catalyst Activity Results for CCS Pilot, July 2003 (measured by Hg SCEM) 4-35

Table 4-18 Oxidation Catalyst Activity Results for CCS Pilot, October and December 2003 (measured by Hg SCEM) 4-36

Table 4-19 February 2004 Oxidation Catalyst Activity Results for CCS Pilot (measured by Hg SCEM) 4-37

Table 4-20 June 2004 Oxidation Catalyst Activity Results for CCS Pilot (measured by Hg SCEM) 4-39
Table 4-21 Results of CCS Catalyst Regeneration Tests 4-42
Table 4-22 Summary of Ontario Hydro Results from CCS, October 2002 (all values represent the average from three individual measurement runs; reported at actual duct concentrations, uncorrected for O_2) 4-44
Table 4-23 Comparison of Ontario Hydro Results with EPRI Mercury Semi-continuous Emissions Monitor Results from CCS, October 2002 (Hg concentrations reported at actual duct concentrations, uncorrected for O_2) 4-45
Table 4-24 Comparison of Ontario Hydro Results with EPRI Mercury Semi-continuous Emissions Monitor Results from CCS, July 2003 (all values corrected to 3% O_2 in flue gas) 4-46
Table 4-25 June 2004 Ontario Hydro Relative Accuracy Results for CCS Pilot Compared to Hg SCEM Results 4-48
Table 4-26 Flue Gas Metals Concentrations at CCS by Method 29 (Pilot Unit Inlet Location) – all values in ppbv (dry gas basis) 4-50
Table 4-27 Flue Gas Halogen Species Concentrations at CCS by Method 26a (Pilot Unit Inlet Location) 4-52
Table 4-28 Flue Gas Sulfuric Acid Concentrations at CCS by the Controlled Condensation Method 4-53
Table 4-29 Summary of Measurements of SO_2 to SO_3 Oxidation Across the SBA #5 and C #6 Catalysts at CCS, July 2003 4-53
Table 4-30 Flue Gas NO_X Concentration Data Using Gas Detection Tubes 4-54
Table 4-31 Summary of Measurements of NO to NO_2 Oxidation Across the Hg^0 Oxidation Catalysts and SO_2 Concentrations at CCS, July 2003 (all measurements by portable CEM) 4-55
Table 4-32 Flue Gas Mercury Concentrations and Speciation at Spruce Plant (measured by Hg SCEM) 4-57
Table 4-33 Summary of ICR Results for Plants Firing Western Coals that have Fabric Filters for Particulate Control 4-57
Table 4-34 September 2003 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM) 4-60
Table 4-35 December 2003 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM) 4-62
Table 4-36 February 2004 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM) 4-62
Table 4-37 May 2004 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM) 4-64
Table 4-38 August 2004 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM) 4-65
Table 4-39 October Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM) 4-66
Table 4-40 April 2005 “End-of-Test” Catalyst Oxidation Activity Data 4-69
Table 4-41 April 2005 “End-of-Test” Catalyst Mercury Breakthrough Data 4-69

Table 4-42 May 2005 Post-regeneration Catalyst Oxidation Activity Data 4-74
Table 4-43 May 2005 Post-regeneration Catalyst Mercury Breakthrough Data 4-74
Table 4-44 Summary of Ontario Hydro Results from Spruce Plant, December 11, 2003 4-76
Table 4-45 Summary of Ontario Hydro Results from Spruce Plant, December 12, 2003 4-77
Table 4-46 December 2003 Ontario Hydro Relative Accuracy Results for Spruce Pilot (mean and 95% confidence interval of three runs, compared to Hg SCEM results from same time period) 4-79
Table 4-47 October 2004 Ontario Hydro Relative Accuracy Results for Spruce Pilot (mean and 95% confidence interval of three runs, compared to Hg SCEM results from same time period) 4-81
Table 4-48 Method 29 Data from Spruce Oxidation Catalyst Pilot Unit Inlet, 9 December 2003 (all values shown in ppbv (dry basis), particulate values shown as equivalent gas-phase concentration) 4-85
Table 4-49 Method 29 Mercury Data from Spruce Oxidation Catalyst Pilot Unit Inlet, 9 December 2003 (all values shown in $\mu g/Nm^3$, particulate values shown as equivalent gas-phase concentration) 4-86
Table 4-50 Mercury Concentration Data at Spruce by Hg SCEM, January 2004 4-87
Table 4-51 Comparison of Stack M29 Data and Hg SCEM Data from FGD Outlet 4-89
Table 4-52 Factors Used to Develop ND Lignite Mercury Control Process Economics 4-91
Table 4-53 Comparison of Base Case Economics for ND Lignite Mercury Control Technologies 4-93
Table 4-54 Comparison of Sensitivity Case Economics for ND Lignite Mercury Control Technologies – No Fly Ash Sales 4-95
Table 4-55 Comparison of Sensitivity Case Economics for ND Lignite Mercury Control Technologies – Palladium Catalyst with Regeneration 4-96
Table 4-56 High Removal Sensitivity Case Economics for ND Lignite Mercury Control – Palladium Catalyst with and without Regeneration 4-99
Table 4-57 Factors Used to Develop Mercury Control Process Economics 4-102
Table 4-58 Comparison of Base Case Economics for Mercury Control Technologies 4-105
Table 4-59 Comparison of Sensitivity Case Economics for Mercury Control Technologies – Palladium Catalyst with Regeneration 4-107

1
INTRODUCTION

This document describes the results of a test program co-funded by EPRI and the U.S. Department of Energy's National Energy Technology Laboratory (DOE-NETL), as part of Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems." The process under development uses catalyst materials to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. The oxidizing species are already present in the flue gas and may include chlorine, hydrochloric acid (HCl) and oxygen, and/or other species. Oxidized mercury is removed in the wet FGD absorbers and leaves with the byproducts from the FGD system.

The objective of the project was to test catalysts identified as being effective in a previous DOE-NETL co-funded project, but at a larger scale and in a commercial form so as to provide engineering data for future full-scale designs. The pilot-scale tests were conducted over a period of at least 14 months at each of two sites to provide longer-term catalyst life data.

Based on information from the U.S. Environmental Protection Agency's Mercury Information Collection Request (ICR), the technology under development would have the greatest effect on the flue gas from subbituminous coal or lignite, where most of the mercury is present in the elemental form[1]. There are approximately 28,000 MW of scrubbed capacity firing these fuels, with more systems planned due to new generating capacity coming on line and as a result of the Clean Air Interstate Rule and the Clean Air Visibility Rule recently promulgated by the U.S. EPA.

The project team includes URS Corporation (contracted to the federal government as URS Group, Inc.) as the prime contractor, and EPRI as a team member and co-funder. EPRI has funded and managed mercury emissions measurement and control research since the early 1990s, and funded the initial development of the catalytic oxidation process. Two utilities are also team members and provide co-funding, technical input, and host sites for testing. These utilities are Great River Energy (GRE), which fires North Dakota lignite at their Coal Creek Station (CCS) and City Public Service of San Antonio (now CPS Energy), which fires a Powder River Basin (PRB) subbituminous coal at their J.K. Spruce Plant (Spruce). These two host sites each have existing wet FGD systems downstream of high-efficiency particulate control devices.

This final report summarizes the results of the pilot-scale testing efforts both sites, GRE's CCS and CPS Energy's Spruce Plant.

Process Overview

Figure 1-1 illustrates a simplified process flow diagram for the catalytic oxidation process under development. The process is very straightforward, with no "moving parts." A catalyst material, most likely in a honeycomb form, is inserted into the flue gas path upstream of the FGD system. The outlet of the plant's cold-side particulate control device is the most likely location for such a catalyst, for two reasons. One is that the flue gas velocity is typically low as it exits a particulate control device (e.g., about 5 ft/sec [1.5 m/s] for an electrostatic precipitator [ESP]). This low velocity provides ideal conditions to operate a catalyst at longer residence time and lower pressure drop. The other is that with the flue gas being relatively particulate-free at this location, a small-pitched catalyst can be used. This allows for a high surface area per volume of catalyst relative to "dirty" gas operation, as is typical of selective catalytic reduction (SCR) systems used for NO_X control in coal-fired applications, and allows a smaller catalyst volume to be used. Based on data collected as part of the previous DOE-NETL co-funded project mentioned above, it was anticipated that only a 6-in. to 12-in. (15- to 30-cm) depth of a small-pitched catalyst would be adequate to achieve greater than 90% oxidation of the elemental mercury present in the flue gas at this location.[2]

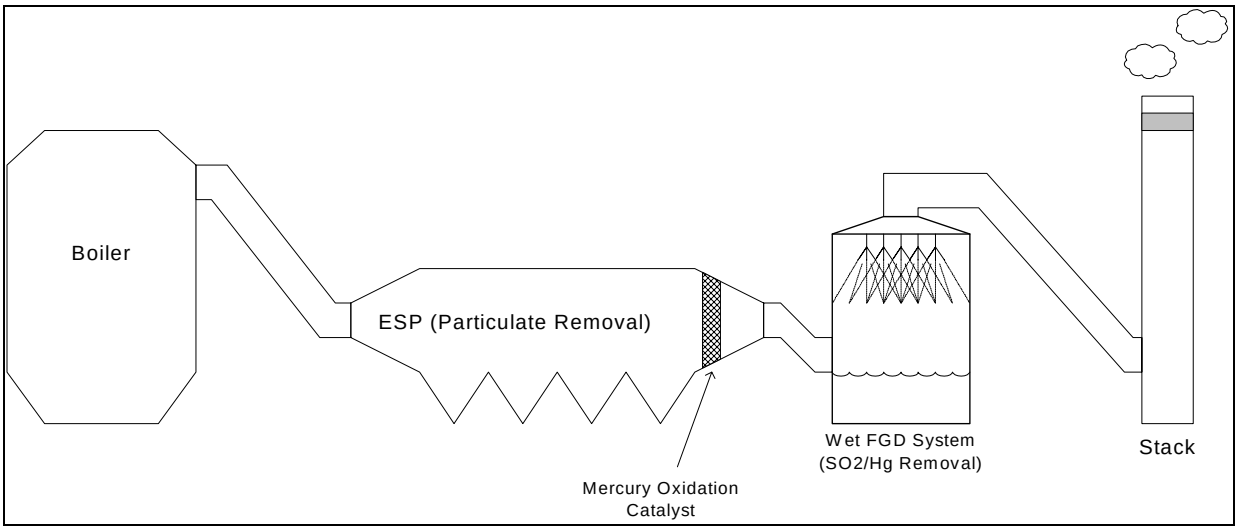

Figure 1-1
General Process Flow Diagram for the Mercury Catalytic Oxidation Process

Downstream of the catalyst, the oxidized mercury is scrubbed in the FGD absorber. For most FGD systems, the mercury removed primarily leaves with the calcium sulfite or gypsum byproduct solids.

Preliminary economic estimates developed prior to this project showed that a catalytic process, if installed upstream of a wet FGD system, could allow plants so equipped to achieve up to 90% overall mercury control at a cost that is up to 50% less than by injection of activated carbon.[2] However, the actual cost of the catalytic process will depend largely on the catalyst life and required catalyst volume. This project has collected data to allow these parameters to be evaluated for the two coal types mentioned above.

The project pilot tested commercial catalyst forms for periods of over 14 months each at two sites. At each site, four different catalysts were tested in parallel in a divided reactor sized to treat approximately 8000 acfm (13,600 m^3/hr) of flue gas (approximately 2000 acfm [3400 m^3/hr] to each catalyst). This allows enough catalyst in each reactor to avoid "wall affects" that can significantly affect results.

Field testing has been completed at both the CCS site and at Spruce Plant. Results from both sites are presented and discussed in this report. Previous topical reports summarize results from CCS[3] and Spruce[4] individually. This report includes, and in some cases updates, all of the information previous presented in those topical reports.

Report Organization

The report is organized into six sections. Following this introduction is a brief Executive Summary. Then, Section 3 discusses the project experimental approach and describes the pilot unit and other equipment used in the project. Section 4 presents and discusses project results, including results of laboratory testing to select and size catalyst materials, an overview of catalyst procurement efforts, field results from catalyst testing, and preliminary process economics based on the pilot test results. Section 5 provides the conclusions that can be made from the results of mercury oxidation catalyst testing at these two plants, and Section 6 lists the references cited in the previous sections of the report.

2
EXECUTIVE SUMMARY

The mercury control process under development uses catalyst materials in honeycomb form to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. Oxidized mercury is removed in the wet FGD absorbers and leaves with the byproducts from the FGD system. The project is intended to provide engineering data for future full-scale designs. The pilot-scale tests were conducted for at least 14 months at each of two sites to provide longer-term catalyst life data. GRE provided the first host site, at their Coal Creek Station (CCS), which fires North Dakota lignite, and City Public Service of San Antonio (now CPS Energy) provided the second site, at their Spruce Plant, which fires Powder River Basin coal.

Mercury oxidation catalyst testing began at CCS in October 2002, with only two of the four catalyst chambers occupied with catalyst materials. In December 2002, a third catalyst was installed, and the fourth was installed in early June 2003. The CCS pilot unit operated with all four catalysts in service through the end of June 2004.

An important finding during these tests was that, even though the mercury oxidation catalyst pilot unit was installed downstream of a high-efficiency ESP at CCS, fly ash builds up over time and began to plug flue gas flow through the horizontal catalyst cells. Sonic horns were installed in each catalyst compartment and appeared to limit fly ash buildup, at least for the three catalysts of most interest for process commercialization.

Over nearly 21 months of operation, a palladium-based catalyst slowly declined in activity, with initial elemental mercury oxidation percentages of 95% across the catalyst, but declining to 67% at the end of the period. A carbon-based catalyst began with almost 98% elemental mercury oxidation across the catalyst, but declined in activity to achieve about 79% oxidation after nearly 13 months in service.

The other two catalysts were less active. An SCR-type catalyst (titanium/vanadium) declined from an initial value of 67% to only 26% elemental mercury oxidation after nearly 21 months in flue gas service, while an experimental fly-ash-based catalyst declined to only 12% oxidation after nearly 17 months. The fly-ash-based catalyst was not cleaned effectively by the sonic horn as described above, so the loss of activity observed may be exacerbated by the buildup of CCS fly ash deposits in the horizontal catalyst cells.

The palladium-based and SCR-type catalysts were effectively regenerated at the end of the long-term test by flowing 600^{o}F air at a slow rate through the catalyst overnight, with much of their original activity for elemental mercury oxidation being restored. The carbon-based catalyst was

not observed to regenerate at this temperature. No attempt was made to regenerate the fly-ash-based catalyst due to the observed fly ash buildup within the catalyst cells.

Preliminary process economics were developed for the palladium-based and carbon-based catalysts for a scrubbed, North Dakota lignite application. As described above, the pilot-scale results showed the catalysts could not sustain 90% or greater oxidation of elemental mercury in the flue gas for a period of two years. Consequently, the economics were based on performance criteria in a later DOE NETL solicitation, which required candidate mercury control technologies to achieve at least a 55% increase in mercury capture for plants that fire lignite. These economics show that if the catalysts must be replaced every two years, the catalytic oxidation process is 30 to 40% less costly than conventional activated carbon injection if the plant currently sells their fly ash, and would lose those sales with carbon injection. If the plant does not sell their fly ash, activated carbon injection was estimated to be slightly more cost effective. There was little difference in the estimated cost of the process for palladium versus the carbon-based catalysts.

However, if the palladium-based catalyst can be regenerated to double its useful life to four years, the catalytic oxidation process economics are greatly improved. With regeneration, the catalytic oxidation process shows a 24% to over 50% reduction in mercury control cost compared to activated carbon injection, depending on whether or not the plant sells its fly ash and on what is assumed for regeneration costs.

At the second site, Spruce Plant, mercury oxidation catalyst testing began in September 2003, with only two of four chambers occupied with catalysts. In November 2003, the third and fourth catalysts were installed. The Spruce pilot unit operated with all four catalysts in service through the end of April 2005, interrupted only by a host unit outage in late February/early March 2005.

In the previous testing at CCS, even though the mercury oxidation catalyst pilot unit was installed downstream of a high-efficiency ESP, fly ash tended to build up over time and began to plug flue gas flow through the horizontal catalyst cells. Sonic horns were installed in each catalyst compartment and appeared to limit fly ash buildup. However, at Spruce, with a baghouse upstream of the catalysts, sonic horns did not appear to be necessary and were never installed. Pressure drop across the four catalysts remained below 1 in. H_2O (0.25 kPa).

Catalyst activity for elemental mercury oxidation was difficult to evaluate at this site, due to the effects of the baghouse upstream of the oxidation catalyst pilot unit. It was found that the baghouse effectively oxidized elemental mercury in the flue gas, with the baghouse outlet flue gas averaging 81% mercury oxidation. The observed range was 60% to greater than 90% oxidation. This oxidation resulted in little elemental mercury remaining in the flue gas going to the oxidation catalyst pilot unit. In many instances, catalyst outlet elemental mercury concentrations were near detection limits for the measurement methods employed (i.e., well below 1 $\mu g/Nm^3$), so the mercury oxidation percentages across the catalyst are uncertain.

In the latter half of the test period, more sensitive mercury semi-continuous emissions monitors (SCEMs) that are able to reliably measure flue gas elemental or total mercury concentrations below 1 $\mu g/Nm^3$ were used to evaluate catalyst performance, with more consistent results. These results showed that two catalyst types (palladium and gold) were more active for elemental

mercury oxidation through the end of the test period than the other two, an experimental carbon-based catalyst and an SCR-type catalyst. The palladium catalyst achieved greater than 90% elemental mercury oxidation across the catalyst in May 2004, after approximately 8 months of service, and 51% oxidation in April 2005, after 18 months in service. This represents more rapid activity loss than was measured for the palladium catalyst at CCS, where it still achieved 67% elemental mercury oxidation after nearly 21 months of service.

The gold catalyst was achieving 47% oxidation in April 2005, also after 18 months of service. The other two catalysts were less active, with an experimental carbon-based catalyst achieving less than 10% oxidation (measured in February 2005) and an SCR-type catalyst achieving 29% oxidation.

At the end of the long-term test period, all four catalysts were observed to regenerate in activity after treatment with heated air overnight. The most active, palladium catalyst improved from 51% elemental oxidation across the catalyst prior to regeneration to 84% oxidation after. The regeneration conditions were similar to those used at CCS. More work is needed to optimize catalyst regeneration conditions to ensure maximum activity in the regenerated catalysts.

Cost estimates were developed for applying the oxidation catalyst technology to a power plant that fires PRB coal and that has a baghouse for particulate control followed by a wet FGD system. The oxidation catalyst cost was estimated for a design that would achieve a minimum of 75% oxidation of the elemental mercury in the baghouse outlet flue gas, which corresponds with 90% or greater overall mercury oxidation in the flue gas going to the wet FGD system and 82% or greater overall mercury capture. While the 90% overall mercury oxidation level corresponds with one of the original project goals, the 82% overall mercury capture level falls short of the original project goal of 90% overall capture. This goal was lowered to reflect observations while the project was in progress that wet FGD systems may not achieve near 100% net capture of oxidized mercury in the flue gas treated, which was the assumption when the original project goal was set. These cost estimates were compared to estimates for conventional (not chemically treater) activated carbon injection upstream of the baghouse, designed to achieve 82% overall mercury capture (including capture by the downstream FGD system).

In this comparison, the cost of oxidation catalyst technology was estimated to be greater than the costs for an activated carbon injection system with similar overall mercury capture performance. For a case where the plant sells it fly ash, and the catalyst is replaced every year, the catalytic oxidation process was over two and a half times the estimated cost of the activated carbon injection process. If the catalyst can be regenerated annually to extend its life to four years, the oxidation process was still estimated to be 36% more costly than activated carbon injection.

However, it was determined that a plant configuration with a baghouse rather than an ESP for particulate control was particularly advantageous for the activated carbon injection process and disadvantageous for mercury oxidation catalysts. It is expected that a cost comparison for a PRB-fired plant with an ESP would be much more favorable for oxidation catalyst technology.

3
EXPERIMENTAL

This section describes the experimental approach used to conduct this project. First, a project overview is provided. Then details are provided regarding the host sites, a mercury semi-continuous emissions (Hg SCEM) monitor used to quantify oxidation catalyst performance, and the oxidation catalyst pilot unit.

Project Overview

The pilot reactor treats low-dust flue gas from downstream of the existing ESP (CCS) or baghouse (Spruce), isokinetically extracted from the host unit's induced draft (ID) fan outlet duct. The treated flue gas returns to the host unit's ID fan inlet, thus avoiding the need for a fan on the pilot unit. The pilot unit is heat traced to maintain temperature (negating heat losses from the relatively small-scale equipment), and is instrumented for temperature, pressure drop and flow rate measurements for each catalyst bed. The gas flow rate through each catalyst bed is controlled independently.

Figure 3-1 shows a simplified piping and instrument diagram (P&ID) for the pilot unit. The pilot unit is perhaps more complex than a future full-scale implementation might be, because it has provisions to measure and control flue gas flow rate and measure mercury species concentrations across each chamber. The full-scale implementation may not require any instrumentation or controls other than monitoring gas pressure drop across the catalyst.

The project concept is to install and operate the pilot unit in the location described, with different catalyst materials in each of the four catalyst chambers. Candidate catalysts were first screened for activity in URS' mercury laboratory, using synthetic flue gases that simulate the compositions at each host site.

At each site, the host utility places the skid near an ID fan, then runs 20-in. (0.51-m) insulated ductwork to the pilot skid inlet and 12-in. (0.30-m) ductwork from the skid outlet to the ID fan suction. The inlet ductwork includes a 5-ft-long "isokinetic scoop" that protrudes into the host unit duct to ensure that a representative gas sample is extracted to the pilot unit. Other than ductwork, the only hookups are electric power for the heat tracing and instrumentation; compressed air for the control valves and Hg SCEM (described below); and a telephone line for data transmittal.

After startup and check out of the pilot unit, the catalysts are installed in the pilot unit. Flue gas flow rates and temperatures are established and placed in automatic control, and the unit is left to operate for several days to allow the catalyst materials to come to mercury adsorption

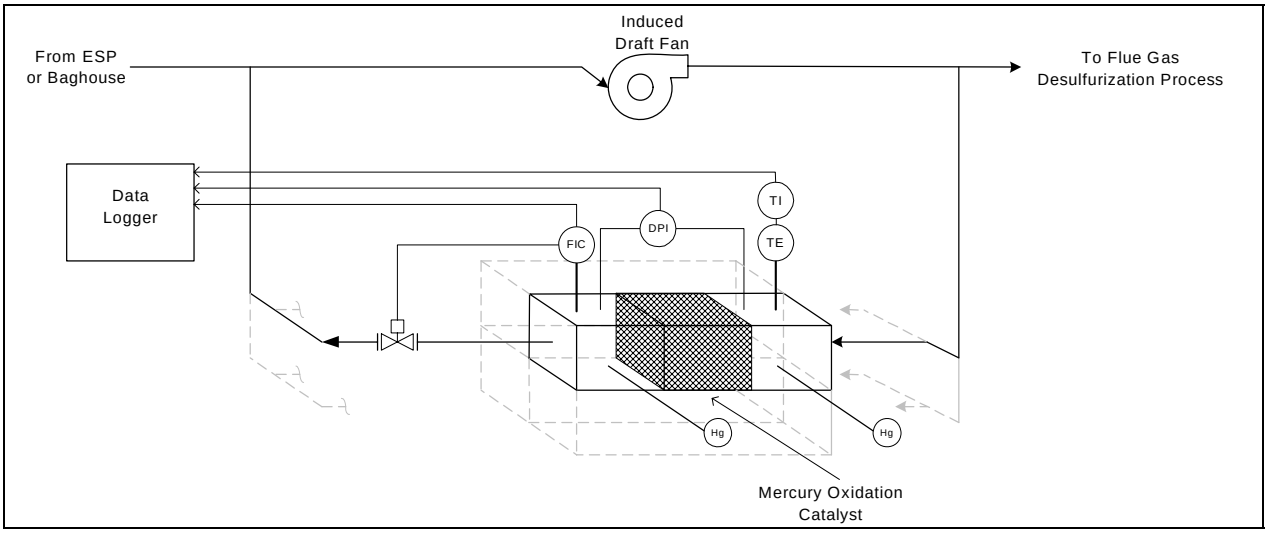

Figure 3-1
Simplified P&ID for the Catalyst Pilot Unit (one of four catalyst chambers shown)

equilibrium. After that period, initial catalyst performance data are collected for each catalyst. The flue gas flow rate through each chamber is varied to allow a determination of catalyst performance versus area/space velocity. The results of these tests are used to determine the ideal area velocity for testing each catalyst. The ideal area velocity is low enough to achieve high elemental mercury oxidation efficiency (preferably greater than 90%), but not so low that a large excess of catalyst is present (e.g., nearly 100% Hg^0 oxidation).

Once the optimum flue gas flow rate for each is established, the pilot unit is left in automated operation at each site for at least 14 months. Telemetry equipment allows pilot unit operating data (flow rate, temperature, and pressure drop) to be monitored from off site. Some control parameters can also be adjusted from off site.

The pilot unit is automated for all operations except mercury analyses, as described below. Other than checking flue gas flow rates and temperatures while team members are on site or by telemetry between site visits, no routine operator intervention is typically required.

Periodically (typically once every one to two months), project team members travel to the site and use an EPRI Hg SCEM to track total and elemental mercury concentrations upstream and downstream of each catalyst, to determine oxidation activity. The Hg SCEM is described later in this section. Periodically over the test period, manual flue gas measurements are conducted using the Ontario Hydro method (ASTM D6784-02) to verify results from the semi-continuous analyzer. At least once during the 14-month period, measurements are made for sulfuric acid and NO_2 concentrations upstream and downstream of each catalyst to quantify whether the oxidation catalysts also oxidize any of the flue gas SO_2 or NO. Significant oxidation of either would be undesirable.

At the beginning of testing at each site, a thorough characterization of the flue gas at the host site ID fan outlet is conducted. This includes mercury concentrations and speciation by the Ontario Hydro method, flue gas sulfuric acid concentration by the Controlled Condensation method, HCl, chlorine, HF, and fluorine by Method 26a, and trace metals by Method 29. Mercury concentration measurements are also being conducted at the host unit FGD outlet, so the removal of mercury by species across the existing scrubber can be quantified.

At the end of the catalyst test period (up to 21 months at CCS and over 17 months at Spruce Plant) final performance measurements are made. The same measurement cycle as described above was conducted at both CCS and Spruce Plant, using two nearly identical pilot units.

Project Host Sites

The two host sites selected for this project, GRE's CCS and CPS Energy's Spruce Plant, each fire relatively low-sulfur, low-chloride coals. CCS fires North Dakota lignite with about a 6300 Btu/lb (3500 kg-cal/kg) heat content, 0.7 wt% sulfur content, 0.1 ppm mercury content, and less than 100 ppm chloride content. Spruce fires a Wyoming, PRB subbituminous coal with about an 8400 Btu/lb (4700 kg-cal/kg) heat content and 0.5 wt% sulfur content. The mercury and chloride contents of the Spruce coal are similar to those at CCS (0.1 ppm mercury and less than 100 ppm chloride). Spruce has occasionally co-fired some petroleum coke along with the PRB coal, although none was fired during the current pilot unit testing.

The two sites are somewhat similar in equipment configuration. Both have tangentially-fired boilers rated at about 550 net MW (two units of this size at CCS, only one at Spruce). CCS has a relatively large, cold-side ESP for particulate control, followed by ID fans and an Alstom (was CE) wet lime FGD system. The FGD absorbers (open spray towers) operate at about 90% SO_2 removal efficiency. About 25% of the flue gas at the ID fan exit bypasses the FGD system, producing a bypass reheat effect. At Spruce, a reverse-gas fabric filter (baghouse) is used for particulate control, followed by ID fans and an Alstom natural oxidation, wet limestone FGD system. As at CCS, the absorbers are designed to achieve about 90% SO_2 removal, and a portion of the ID fan exit gas bypasses the FGD system. The CCS FGD system produces a calcium sulfite byproduct that is landfilled, while the Spruce FGD system produces a naturally oxidized gypsum byproduct that is sold for cement production.

Hg SCEM

The EPRI Hg SCEM is illustrated in Figure 3-2. The analyzer is based on the amalgamation of elemental mercury with gold, and the cold-vapor atomic absorption of elemental mercury that is subsequently thermally desorbed from the gold. Using a liquid-phase gas conversion system, the analyzer can determine a). total mercury concentrations by reducing all of the oxidized mercury to the elemental form with stannous chloride upstream of the gold, or b). elemental mercury concentrations by using either a tris(hydroxy-methyl)aminomethane (Tris) or potassium chloride (KCl) solution to capture oxidized mercury while allowing elemental mercury to pass through without being altered.

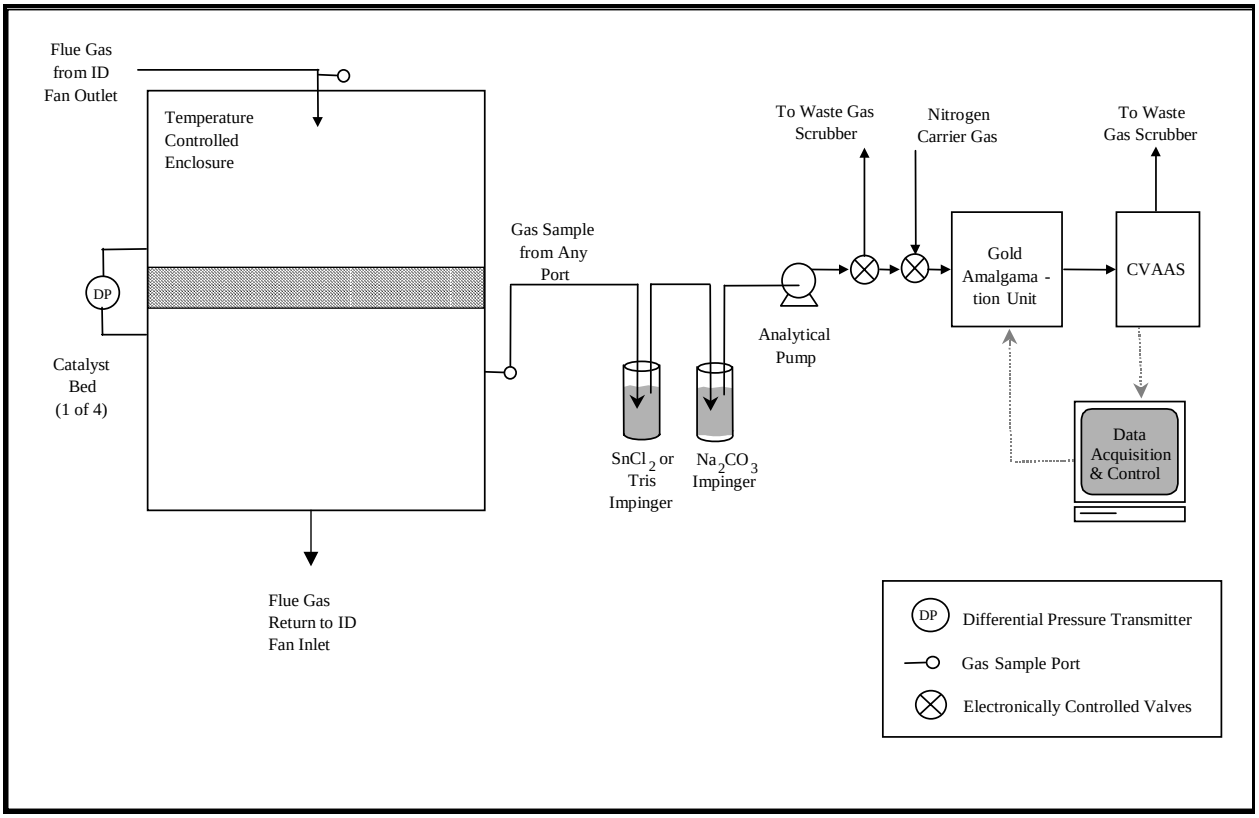

Figure 3-2
Schematic of EPRI Semi-continuous Mercury Analyzer

The development of the Hg SCEM has allowed the performance of various catalyst materials to be determined efficiently and cost effectively. Use of the analyzer on previous projects determined the importance of using only certain materials such as quartz, Teflon®, or Teflon®-lined materials to handle flue gas samples to be analyzed for mercury content. The results of this experience are reflected in the current SCEM design and materials of construction.

At Spruce Plant, the host unit baghouse upstream of the catalyst pilot unit had two adverse effects on the ability to measure oxidation catalyst performance. One was that it oxidized a significant percentage of the elemental mercury present in the flue gas at the air heater outlet location. This led to low inlet elemental mercury concentrations at the catalyst pilot inlet, sometimes less than 1 $\mu g/Nm^3$. The other adverse effect was that the total mercury concentrations and mercury oxidation to the pilot unit were variable. This was apparently due to mercury removal and oxidation across the baghouse, which varied over the baghouse cleaning cycle (less removal and oxidation with clean bags, increasing removal and oxidation as the filtercake built up on the bags). This relationship was observed late in the project when an Hg SCEM was used to monitor the catalyst pilot unit inlet flue gas over a period of several days. It became apparent that the pilot unit inlet flue gas mercury concentration and oxidation varied on nominally the same cycle as baghouse cleaning.

Details of the Hg SCEM designs went through some evolutionary changes over the course of this project. Early versions of the Hg SCEM used a less sensitive atomic absorption spectrophotometer than later versions. This impacted the ability to accurately measure flue gas mercury concentrations of 1 $\mu g/Nm^3$ or lower, particularly elemental mercury concentrations at catalyst outlet measurement locations. It is possible to measure very low mercury concentrations by increasing the cycle length on the semi-continuous analyzer (i.e., more time collecting mercury from the sample gas onto the gold). However, poorer signal-to-noise ratios on early Hg SCEM variations made the accuracy of measurements of mercury concentrations of 1 $\mu g/Nm^3$ or lower questionable. In later Hg SCEM variations, improved signal-to-noise ratios made it possible to measure concentrations of less than 0.5 $\mu g/Nm^3$ with greater confidence. This compares favorably with the Ontario Hydro Method, which has a stated lower measurement limit of 0.5 $\mu g/Nm^3$.[5]

Hg SCEM lower detection limits were important at Spruce, because of the often low inlet elemental mercury concentrations at the catalyst pilot unit inlet as mentioned above. As described in the Results section later in this report, it is believed that some variations in measured oxidation catalyst performance during early testing at Spruce were caused by difficulties in quantifying extremely low catalyst outlet elemental mercury concentrations. A change to Hg SCEMs with more sensitive (i.e., improved signal-to-noise ratio) atomic absorption spectrophotometers mid-way through the test program is believed to have improved the ability to quantify catalyst performance at Spruce.

Oxidation Catalyst Pilot Unit Description

The pilot units used at each site have four catalyst chambers, each representing a cube that is nominally one meter in all three dimensions. Each “cube” has a removable side panel that provides full access to the chamber for installing and retrieving catalysts. The amount of catalyst in each chamber can be varied as necessary to achieve desired elemental mercury oxidation, with the amounts needed based on laboratory screening results. For catalysts where the cross-section of the honeycomb installed is less than one meter by one meter, a “picture frame” spacer is installed around the catalyst block to fit snugly against the chamber side, top and bottom walls. This spacer centers the catalyst block in the chamber and reduces the effective chamber open area to ensure that all of the flue gas flows through the honeycomb and not through the annular space between the honeycomb and chamber walls.

The design flue gas flow rate through each chamber is 2000 acfm (3400 m^3/hr), for a total of nominally 8000 acfm (13,600 m^3/hr) to the skid. The normal flue gas flow rate range through each catalyst compartment is 1500 to 2500 acfm (2550 to 4250 m^3/hr).

Figure 3-3 summarizes the mechanical design of the pilot unit skid. The skid inlet piping is 20-in. (0.51-m) diameter pipe, and the return to the utility ID fan inlet duct is 12-in. (0.30-m) pipe. On the inlet side of the chambers, the 20-in. (0.51-m) common feed pipe splits to a 10-in. (0.25-m) diameter feed pipe for each followed by a 30^o transition to each cube opening. The low velocity in the 10-in. (0.25-m) line and the shallow angle on the 30^o transition are intended to ensure good flue gas flow distribution across the face of each catalyst. On the outlet side the

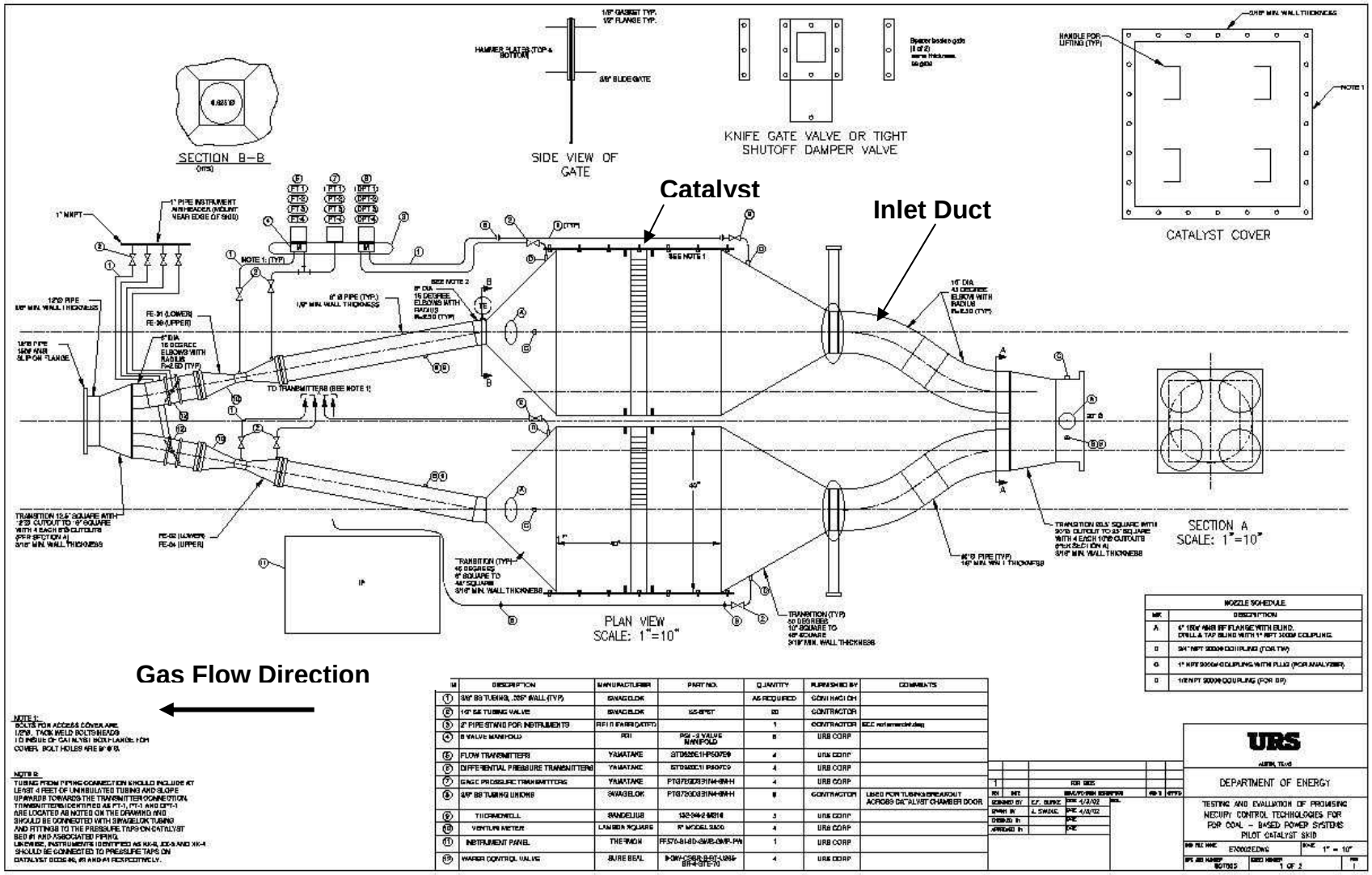

Figure 3-3
Plan View of Final Catalyst Pilot Unit Design

transition is much steeper, at 45°, and the outlet piping is also smaller at 6-in. (0.15-m) diameter. The smaller diameter is to increase the gas velocity, to improve the signal strength for the venturi flow meters in the outlet run from each chamber. Butterfly-style dampers are used to control flue gas flow. Damper position is automatically modulated to control flow rate based on feedback from the venturi flow meter pressure differential, corrected for the total gauge pressure and measured gas temperature in the outlet duct.

The pilot unit inlet gas is pulled from a 5-ft-long (1.5-m) "scoop" installed through the duct wall at the host unit's ID fan outlet. The "scoop" is a straight piece of pipe cut at a 45° angle at the end, with the open area facing into the flue gas flow, to result in pulling gas at approximately isokinetic conditions. The 5-ft length is to ensure a representative gas sample is extracted from near the center of the duct rather than along the duct wall. The pilot unit can be isolated from the host unit with wafer-style butterfly dampers at the pilot unit inlet penetration on the ID fan outlet duct and return penetration on the ID fan inlet duct. Each individual catalyst chamber or cube can be isolated by closing the flow control damper on the outlet side and a shop-built manual knife gate valve at the inlet to that chamber.

The pilot unit instrumentation is summarized in Table 3-1. The pilot unit has a total of five control loops. Four are for flow rate through the individual catalyst chambers, as described above, and the fifth is for pilot unit inlet flue gas temperature. The inlet temperature is controlled with heat tracing on the 20-in. [0.51-m] diameter inlet pipe run, to try to match the host unit ID fan outlet gas temperature at full load (nominally 300°F [150°C]). A slight positive offset is required to account for temperature losses across the catalyst enclosures. The pilot unit piping runs and catalyst enclosures are insulated with a 2-in. (5-cm) thickness of fiberglass insulation to minimize heat losses.

Table 3-1
Summary of Pilot Unit Instrumentation

Parameter	Sensor Type	Number of Each
Pilot Unit Inlet Temperature	Type K thermocouple	1
Catalyst Outlet Temperature	Type K thermocouple	1 per chamber (4 total)
Catalyst Pressure Drop	Differential pressure transducer	1 per chamber (4 total)
Catalyst Outlet Gauge Pressure	Differential pressure transducer	1 per chamber (4 total)
Catalyst Flow Rate	Venturi flow meter, Differential pressure transducer (corrected for temperature and gauge pressure)	1 per chamber (4 total)
Pilot Unit Inlet and Catalyst Outlet Hg Concentrations, Speciation	Semi-continuous Hg analyzer	1 (cycled between pilot unit inlet and individual catalyst outlets, for Hg^0 and total Hg)

Mercury concentrations and speciation are measured at the pilot unit inlet and at the outlets of each catalyst chamber with the EPRI Hg SCEM, which was described previously in this section.

The analyzer is cycled between the five measurement locations, and between measuring elemental mercury and total mercury to determine the elemental mercury oxidation across each catalyst. In some instances two Hg SCEMs were used, with one monitoring pilot unit inlet gas conditions and the second cycling between the outlet flue gas from each of the four catalyst chambers.

The fabrication of the first, DOE co-funded pilot unit was completed in July 2002 and it was shipped to CCS in North Dakota in August. Figures 3-4 through 3-6 are photographs that the pilot unit as it was being fabricated. Great River Energy installed the pilot unit near the induced draft (ID) fans on Unit 1 at CCS, with the flue gas going to the pilot unit being withdrawn from one ID fan outlet duct and returning to the inlet duct on an adjacent fan. The installation was completed in late August 2002. Figure 3-7 shows the completed pilot unit as installed at CCS. This photograph was taken before the pilot unit inlet and outlet duct runs were insulated, and before a temporary shed was constructed around the pilot unit to protect it from the weather.

Figure 3-4
Photograph of the Pilot Skid from the Side on the Inlet End, Near the Completion of its Mechanical Fabrication

Figure 3-5
Photograph of the Pilot Skid from the Exit End, Near the Completion of its Mechanical Fabrication

Figure 3-6
Photograph of Pilot Unit Control Panel Prior to Installation on Pilot Skid

Figure 3-7
Pilot Skid as Installed at CCS

The fabrication of the second pilot unit was funded by EPRI, to allow testing to proceed at both sites simultaneously. Fabrication of that pilot unit was completed in the spring of 2003, and it was shipped to Spruce Plant in San Antonio. CPS installed the pilot unit near the west ID fan, with the flue gas going to the pilot unit being withdrawn from the ID fan outlet duct and returning to the inlet duct. The installation was completed in late August 2003. Figure 3-8 shows the completed pilot unit as installed at Spruce Plant.

Figure 3-8
Pilot Skid as Installed at Spruce Plant

Laboratory Catalyst Screening Apparatus

Prior to selecting catalysts for testing in the pilot units, sample cores of candidate catalysts were tested on a bench-scale apparatus in URS' Austin, Texas laboratories. In the bench-scale apparatus, a synthetic flue gas is mixed from bottled gases. The synthetic flue gas typically contains nitrogen, oxygen, moisture, CO_2, SO_2, NO_X, and HCl. The proportions of each are adjusted to best match flue gas conditions at the power plant being simulated. The moisture is added by sending a portion of the nitrogen through a saturator that operates at elevated temperature. The gases are mixed to achieve a total gas flow rate of approximately 0.6 to 1.3

L/min (measured at room temperature), then heated to the desired synthetic flue gas temperature, typically in the range of 250°F to 350°F. Elemental mercury is added to the flue gas by passing a small percentage of the dry nitrogen through a permeation tube.

Once mixed, the synthetic flue gas flows through a small catalyst holder, which is heat traced to maintain the target flue gas temperature. In the catalyst holder, catalyst cores of approximately 5/8-in. diameter and up to 2 inches in length are placed for exposure to the synthetic flue gas. Flue gas exiting the catalyst holder is vented to atmosphere through a series of scrubbers to remove acid gases and mercury.

A mercury SCEM, similar to what is described above, is used to monitor the catalyst inlet and outlet flue gas for mercury concentration. At the beginning of a test, flue gas is flowed over the catalyst core and the outlet flue gas mercury concentration is monitored until the catalyst has achieved mercury adsorption equilibrium (i.e., the catalyst outlet total mercury concentration is equal to the inlet total mercury concentration). This may take a day or longer of continuous flue gas exposure to achieve. Once equilibrium has been achieved, the catalyst outlet flue gas is measured for mercury speciation to determine the catalyst oxidation activity. Measurements are made at several flow rates to determine activity as a function of space velocity or area velocity.

Because the catalyst sample cores vary in specific surface area and in mercury oxidation activity, the catalyst core length often has to be adjusted to achieve mercury oxidation percentages in the desired range of approximately 80 to 95+% oxidation across the core. Lower oxidation percentages are below the range of interest, and higher oxidation percentages make it difficult to measure space/area velocity effects. If results from the first series of tests with a catalyst lie outside this desired range, the core length is typically adjusted and the tests are repeated.

4
RESULTS AND DISCUSSION

This section is divided into five subsections. The first describes the results of laboratory tests conducted to select and size catalysts for each pilot unit, and the second describes the catalyst procurement effort. The third subsection discusses pilot unit operation at CCS from October 2002 through June 2004, while the fourth subsection discusses pilot unit operation at Spruce Plant from September 2003 through May 2005. These subsections also present and discuss results from flue gas characterization efforts conducted around the CCS and Spruce pilot units, respectively. The final subsection presents and discusses preliminary process economic estimates.

Laboratory Results

CCS Simulations

At the beginning of the project a list of candidate catalyst materials was developed based primarily on results from a previous DOE-NETL co-funded project. Table 4-1 shows the initial list of catalysts considered. The catalyst materials were expected to include a palladium, an SCR-type catalyst (titanium/vanadium) and an experimental activated carbon on alumina. It was hoped that the fourth catalyst would be a fly-ash-based material fixed on a ceramic substrate, although the use of this catalyst was dependent on identifying a catalyst manufacturer that could bond fly ash material to a honeycomb substrate while retaining high oxidation activity.

Table 4-1
Catalyst Materials Considered for Evaluation in Pilot-scale Mercury Oxidation Tests at CCS

Catalyst Name (Abbreviation)	Description
Palladium #1 (Pd #1)	Commercial palladium catalyst wash coated on alumina substrate
SCR Catalyst (SCR)	Commercial NO_x catalyst; titanium-vanadium based honeycomb
Carbon #6 (C #6)	Experimental carbon on an alumina substrate
Subbituminous Fly Ash #5 (SBA #5)	Active fly ash on an alumina substrate
Alternate Palladium #1 Configuration (Pd #1a*)	Commercial palladium/alumina catalyst; operated at different space velocity or catalyst configuration than Pd #1

* Alternate catalyst; proposed choice if fly ash cannot be successfully fixed to ceramic substrate.

If this had not proven to be possible, another alternative considered was to test the palladium-based material in a different configuration. Alternate configurations might include varied pitch, varied surface area, or an alternate substrate material.

Candidate catalysts were screened for activity in URS' mercury laboratory using synthetic flue gases that approximately simulate the flue gas composition at CCS. Table 4-2 summarizes the simulation gas conditions. The percent moisture is lower than what would be expected in the flue gas from North Dakota lignite (about 15%). The value listed (9%) represents the practical upper limit on the laboratory gas mixing apparatus. This difference in expected actual versus simulation gas moisture content is not thought to affect the results, though.

Table 4-2
Synthetic Flue Gas Conditions for CCS Simulations

Species	Condition
SO_2 (ppmv)	500
NO_X (ppmv)	200
HCl (ppmv)	6
O_2 (%)	5
CO_2 (%)	12
H_2O (%)	9
N_2 (%)	Balance
Temperature (^oF) [^oC]	350 [177]

The catalysts tested included the SCR catalyst, C #6 in a monolithic honeycomb substrate, SBA #5 in a monolithic substrate, and Pd#1 wash coated at several different palladium loadings on a ceramic honeycomb. The results of the laboratory simulation runs for the SCR catalyst, C #6 and SBA #5 are summarized in Table 4-3, and plotted as a function of area velocity in Figure 4-1. The results for Pd #1 samples are discussed later in this subsection. Note that the oxidation results shown in these tables and figures were all measured after the catalysts had reached mercury adsorption equilibrium. Thus, the performance shown truly represents the oxidation of elemental mercury across the catalyst sample and no elemental mercury adsorption.

The results plotted in Figure 4-1 show high oxidation percentages (>90%) for all three catalysts (SCR, C #6, and SBA #5) when tested at the longer core lengths and area velocities of 20 to 60 sft/hr (5.8 to 17 Nm/h). The SCR and C #6 catalysts were also tested at shorter core lengths: 1-in. (2.5-cm) vs. 2-in. (5-cm) for the SCR catalyst, and 0.4-in. (1-cm) vs. 0.8-in. (2-cm) for the C #6 catalyst, to allow operation at higher area velocities. At the shorter core lengths, the oxidation performance of each dropped considerably. It is speculated that at these shorter core lengths, the gas distribution across the face of the honeycomb was adversely affected, lowering the overall oxidation activity from what would have been realized with a more ideal gas distribution.

Table 4-3
Laboratory Simulation Results for SCR, C #6, and SBA #5 Catalysts at CCS Conditions

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
SCR; 2" core	0.64	118	5.01	96
SCR; 2" core	1.0	75.9	3.39	96
SCR; 2" core	1.3	58.4	3.13	95
SCR; 1" core	0.64	110	14.8	87
SCR; 1" core	1.0	70.6	10.1	86
SCR; 1" core	1.3	54.3	9.16	83
C #6; 0.8" core	0.64	84.0	0.94	99
C #6; 0.8" core	1.0	54.1	2.61	95
C #6; 0.8" core	1.3	40.7	1.55	96
C #6; 0.4" core	0.64	50.5	6.66	87
C #6; 0.4" core	1.0	32.5	6.49	80
C #6; 0.4" core	1.3	24.4	6.99	71
SBA #5; 0.6" core	0.64	102	6.77	93
SBA #5; 0.6" core	1.0	66.8	1.00	99
SBA #5; 0.6" core	1.3	50.3	1.53	97

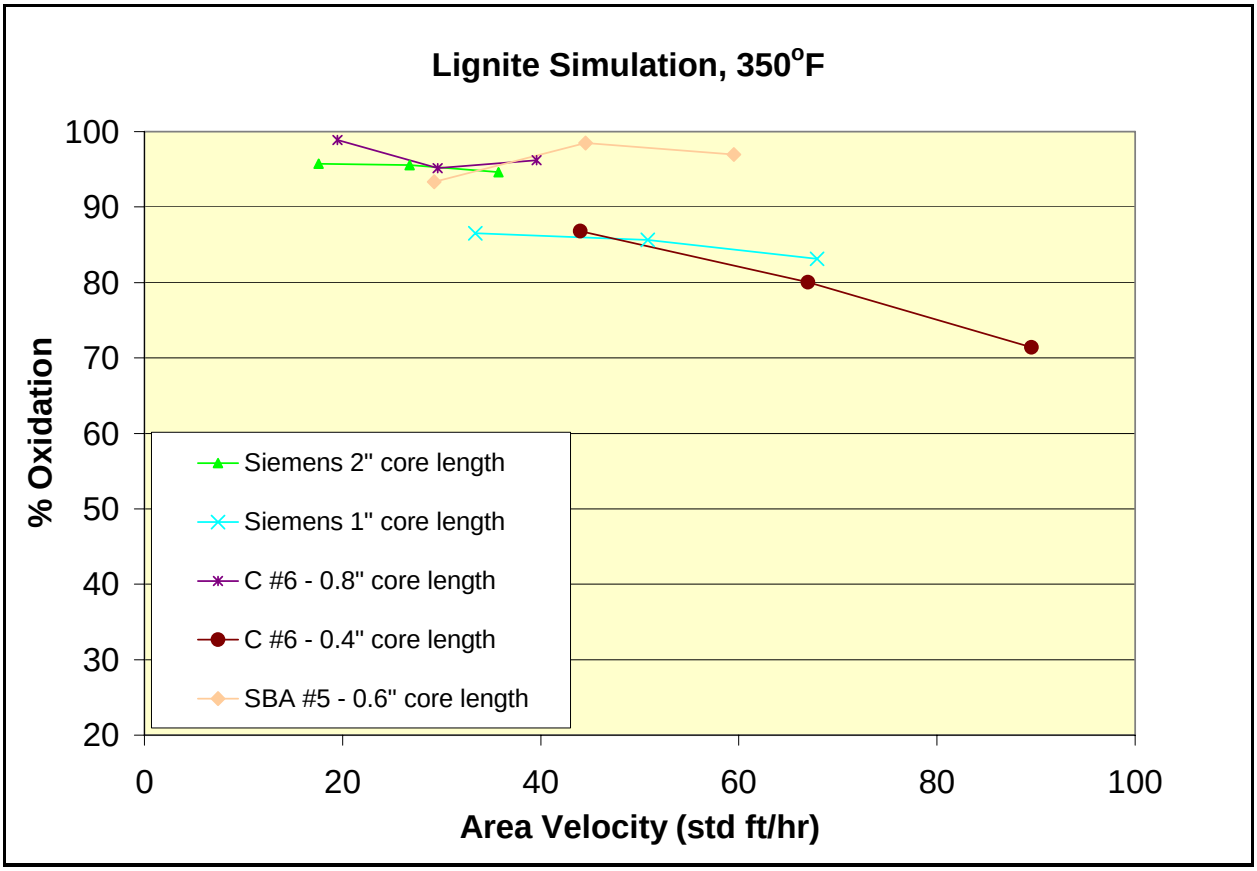

Figure 4-1
Elemental Mercury Oxidation Percentage vs. Area Velocity for SCR, C #6, and SBA #5 Catalyst Samples

This speculation indicates a limitation of the laboratory simulation setup. The catalyst core testing is conducted with an existing apparatus that was set up to test mercury sorbent and catalyst materials in a “sand bed” reactor. To test honeycomb catalyst cores, the sand bed is replaced with a catalyst core of round cross section, typically about 5/8-in. (1.6-cm) diameter. The catalysts tested were acquired from the various vendors in whatever pitch was available.

With the diameter of the catalyst core holder fixed at 5/8-in. (1.6-cm), the core pitch being fixed, and the gas mixing flow rate range of the existing apparatus limited to about 0 to 1.3 l/min, the only variable that can be adjusted to increase area velocity is the core length. As can be seen in Figure 4-1, to achieve higher area velocities (approaching 100 sft/hr [29 Nm/h]) the corresponding core lengths became very short, particularly for the C #6 and SBA #5 catalyst cores, which were available in a very tight cell pitch pattern. In spite of this limitation, the data for the longer core lengths for the SCR catalyst and for the C #6 catalyst were considered to be adequate for determining catalyst quantities for the pilot unit.

Table 4-4 summarizes the results of a number of laboratory runs with Pd #1 catalyst samples, made at two palladium loadings and two core lengths. The palladium loadings are expressed as a factor times a reference (proprietary) base loading. All of the measurements in Table 4-4 were

made using Tris impingers in the semi-continuous mercury analyzer sample train for measuring elemental mercury concentrations in the catalyst outlet simulation gas. Figure 4-2 is a plot of these results. Note that Tris impingers were also used when measuring the results previously presented in Table 4-3 for the other three catalysts.

Table 4-4
Laboratory Simulation Results for Pd #1 Catalyst Samples at CCS Conditions (all using Tris impingers)

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
Pd #1 7x; 2" core	0.64	147	0.01	100
Pd #1 7x; 2" core	1.0	94.9	0.01	100
Pd #1 7x; 2" core	1.3	71.3	0.01	100
Pd #1 5x; 2" core	0.64	118	14.1	88
Pd #1 5x; 2" core	1.0	75.9	6.02	92
Pd #1 5x; 2" core	1.3	57.1	4.59	92
Pd #1 7x; 1" core	0.64	96.6	23.9	75
Pd #1 7x; 1" core	1.0	63.1	20.9	67
Pd #1 7x; 1" core	1.3	47.6	15.9	67
Pd #1 5x; 1" core	0.64	102	68.7	32
Pd #1 5x; 1" core	1.0	66.8	48.7	27
Pd #1 5x; 1" core	0.64	97.7	52.0	47
Pd #1 5x; 1" core	1.0	63.8	31.4	51
Pd #1 5x; 2" core	0.64	39.1	10.9	72
Pd #1 5x; 2" core	1.0	25.5	2.4	91
Pd #1 5x; 2" core	1.3	19.3	4.3	78
Pd #1 5x; 2" core	1.6	15.7	5.2	67
Pd #1 7x; 2" core	0.64	38.1	3.0	92
Pd #1 7x; 2" core	1.0	24.9	0.0	100

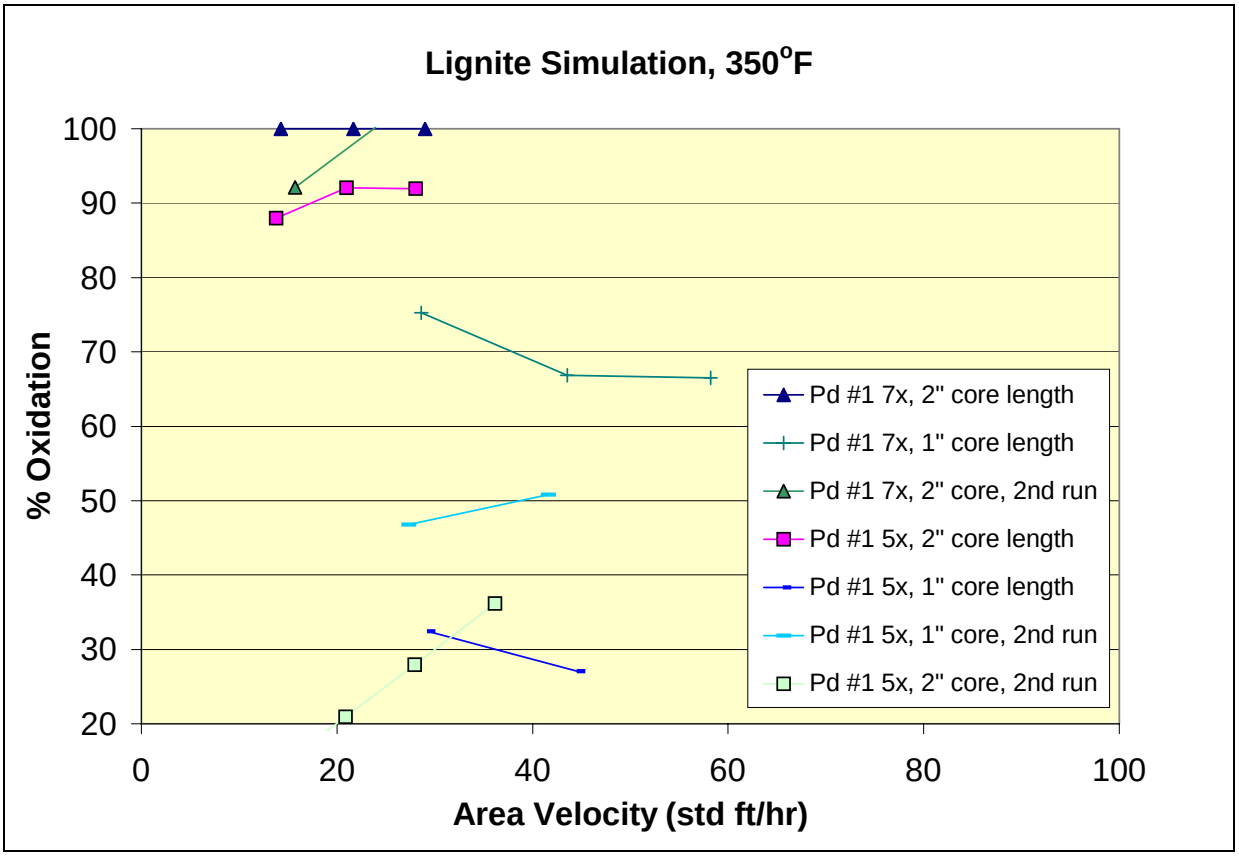

Figure 4-2
Elemental Mercury Oxidation Percentage vs. Area Velocity for Pd #1 Catalyst Samples (all measurements made using Tris impingers)

The results for Pd#1 plotted in Figure 4-2 show a great deal of scatter. Two factors appear to cause this data scatter. One may be the core length issue as described above for the other catalyst types. The 2-in. (5-cm) core length data are probably more representative of the catalyst performance than the 1-in. (2.5-cm) data. Another factor is that there appears to have been an interference between some component in the sample gas exiting the Pd #1 cores and the Tris solution used to remove oxidized mercury from the sample gas. This apparent interference caused a high degree of variability in the measured catalyst outlet elemental mercury concentrations, and thus caused the performance results plotted in Figure 4-2 to be suspect.

Additional tests were conducted with Pd #1 catalyst samples, using potassium chloride (KCl) rather than Tris solution to remove oxidized mercury from the sample gas going to the laboratory mercury analyzer when measuring for elemental mercury. KCl solution is used to capture oxidized forms of mercury in the draft Ontario Hydro gas sampling method and has been shown to produce similar results as the Tris solution in previous URS tests.

These results are summarized in Table 4-5. The apparent interference was eliminated by the solution change, and these new results were used to determine the palladium loading and catalyst volume required for the pilot unit for the Pd #1 catalyst. As shown later in this section, the field results for Pd #1 agreed well with the laboratory results measured using KCl impingers.

Table 4-5
Laboratory Simulation Results for Pd #1 Catalyst Samples at CCS Conditions (all tests with KCl instead of Tris impingers when measuring elemental mercury concentrations)

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
Pd #1 5x; 2" core	0.98	22.3	0.52	98
Pd #1 5x; 2" core	1.3	16.7	0.30	98
Pd #1 5x; 2" core	1.7	12.9	0.00	100
Pd #1 3x; 2" core	0.98	23.6	0.00	100
Pd #1 3x; 2" core	1.3	17.8	0.70	96
Pd #1 3x; 2" core	1.7	13.6	0.32	98
Pd #1 3x; 1" core	0.98	23.4	0.41	98
Pd #1 3x; 1" core	1.3	17.7	1.17	93
Pd #1 3x; 1" core	1.7	13.5	1.31	90

The results summarized in Table 4-5 show consistently high elemental mercury oxidation performance, even with a lower (3x rather than 5x or 7x) palladium loading and at the shorter, 1-in. (2.5-cm) core length. Figure 4-3 plots these new results along with the previous results that were included in Figure 4-2. The new results measured with the KCl impingers show elemental mercury oxidation percentages of 90% even at a relatively high area velocity of 75 sft/hr (22 Nm/h) and the lower, 3x palladium loading on the honeycomb sample.

Table 4-6 shows honeycomb substrate dimensions for each catalyst sample, and the actual versus predicted performance of each compared to a mass transfer model. For the Pd #1 catalyst, only the data collected with KCl impingers are shown in Table 4-6.

The mass transfer model to predict mercury oxidation performance is based on a simplifying assumption that mercury oxidation is instantaneous once the mercury has diffused to the catalyst surface. If the actual performance is close to the model prediction, this is an indicator of very rapid catalytic oxidation at the catalyst surface, whereas if the actual performance is well below the model prediction it is an indicator of a slower surface reaction. The actual versus predicted oxidation is compared on the basis of "number of transfer units" (NTU, $\ln([Hg^0_{in}]/[Hg^0_{out}])$), a mass transfer performance term, rather than on the basis of percent oxidation.

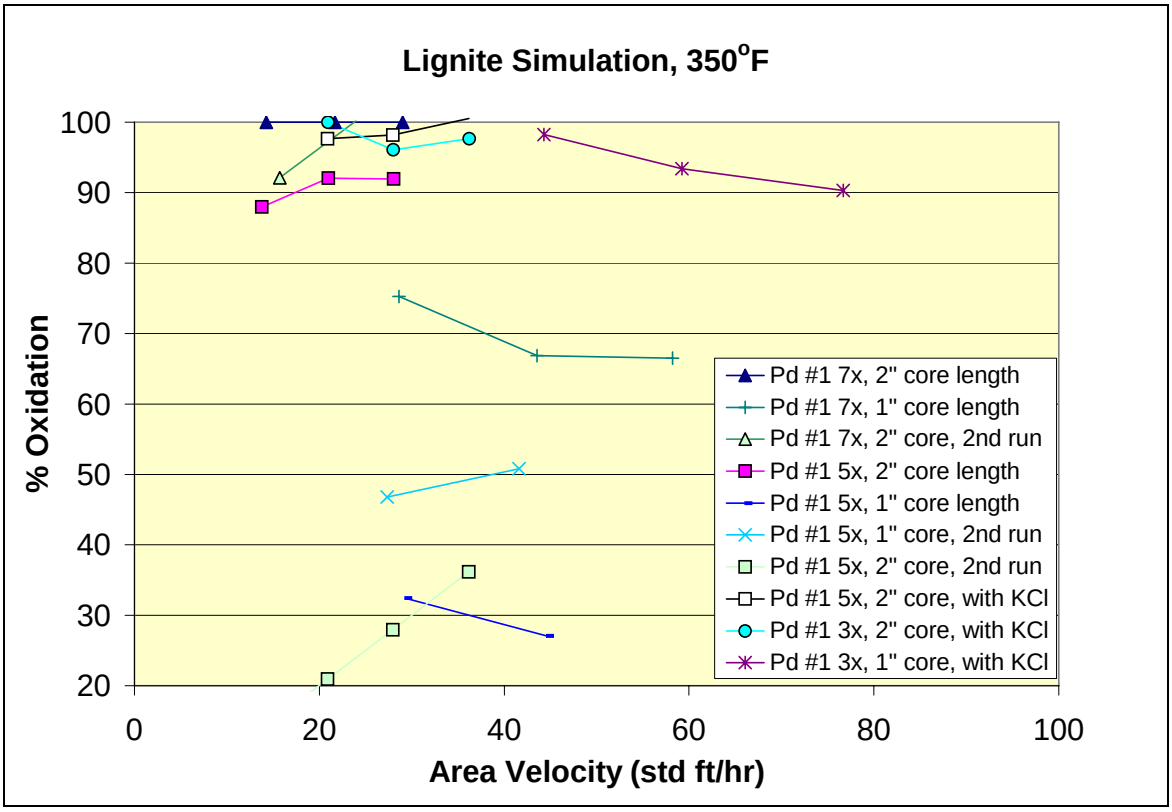

Figure 4-3
Elemental Mercury Oxidation Percentage vs. Area Velocity for Pd #1 Catalyst Samples (all measurements, including those made using Tris and KCl impingers)

Table 4-6
Honeycomb Dimensions and Actual vs. Predicted Catalyst Performance

Catalyst Type (gas flow rate, l/min)	Core Diameter (in) [cm]	Core Length (in) [cm]	Cell Pitch (mm)	Cell Wall Thickness (mm)	Measured Hg^0 Oxidation (%)	Predicted Hg^0 Oxidation (%)	Measured NTU/ Predicted NTU (%)
SCR (0.64)	0.56 [1.4]	2.0 [5.1]	4.15	0.51	96	100*	57
SCR (1.0)	0.56 [1.4]	2.0 [5.1]	4.15	0.51	96	97	88
SCR (1.3)	0.56 [1.4]	2.0 [5.1]	4.15	0.51	95	94	>100
SCR (0.64)	0.56 [1.4]	1.1 [2.8]	4.15	0.51	87	96	64
SCR (1.0)	0.56 [1.4]	1.1 [2.8]	4.15	0.51	86	88	93
SCR (1.3)	0.56 [1.4]	1.1 [2.8]	4.15	0.51	83	81	>100

Table 4-6
Honeycomb Dimensions and Actual vs. Predicted Catalyst Performance (continued)

Catalyst Type (gas flow rate, l/min)	Core Diameter (in) [cm]	Core Length (in) [cm]	Cell Pitch (mm)	Cell Wall Thickness (mm)	Measured Hg^0 Oxidation (%)	Predicted Hg^0 Oxidation (%)	Measured NTU/ Predicted NTU (%)
C #6 (0.68)	0.56 [1.4]	0.82 [2.1]	1.75	0.45	99	100*	39
C #6 (1.0)	0.56 [1.4]	0.82 [2.1]	1.75	0.45	95	100*	37
C #6 (1.3)	0.56 [1.4]	0.82 [2.1]	1.75	0.45	96	100*	51
C #6 (0.68)	0.56 [1.4]	0.36 [0.9]	1.75	0.45	87	100*	38
C #6 (1.0)	0.56 [1.4]	0.36 [0.9]	1.75	0.45	80	98	43
C #6 (1.3)	0.56 [1.4]	0.36 [0.9]	1.75	0.45	71	94	43
SBA #5 (0.63)	0.56 [1.4]	0.58 [1.5]	1.72	0.49	93	100*	30
SBA #5 (1.0)	0.56 [1.4]	0.58 [1.5]	1.72	0.49	99	100*	76
SBA #5 (1.3)	0.56 [1.4]	0.58 [1.5]	1.72	0.49	97	99	75
Pd #1, 3x (1.0)	0.55 [1.4]	2.0 [5.1]	3.17	0.35	100	100*	>100
Pd #1, 3x (1.3)	0.55 [1.4]	2.0 [5.1]	3.17	0.35	96	99	70
Pd #1, 3x (1.7)	0.55 [1.4]	2.0 [5.1]	3.17	0.35	98	97	>100
Pd #1, 3x (1.0)	0.55 [1.4]	1.1 [2.8]	3.17	0.35	98	96	>100
Pd #1, 3x (1.3)	0.55 [1.4]	1.1 [2.8]	3.17	0.35	93	93	>100
Pd #1, 3x (1.7)	0.55 [1.4]	1.1 [2.8]	3.17	0.35	90	87	>100

*Predicted number is less than 100.00 but greater or equal to 99.50; the value is shown as 100 in the table due to rounding.

The mass transfer model was developed from equations found in the literature for mass transfer in a fluid in laminar flow through a circular conduit.[6] An equivalent diameter was calculated from the square honeycomb internal dimensions and appears to work well with the circular conduit equations. The viscosity and diffusivity of elemental mercury and mercuric chloride in flue gas, which are required for these calculations, were estimated using methods taken from Reid, Prausnitz and Poling.[7]

Table 4-6 includes the dimensions of the various honeycomb core samples. This table illustrates why the catalyst performance was plotted as a function of area velocity rather than space velocity. The cores supplied are on substrates with varying cell pitches and wall thickness, and thus varied active surface area per unit volume. Space velocity is defined as the standard gas

flow rate divided by the catalyst volume, but at similar space velocities the smaller-pitched catalysts would have more active surface areas than the coarser-pitched catalysts. The area velocity is defined as the standard gas flow rate divided by the catalyst external surface area, and thus better accounts for varied cell pitch and wall thickness. Since any of the catalyst materials could conceivably be applied at any substrate cell pitch, the area velocity is the more equitable parameter for catalyst comparison, and less influenced by the cell pitch at which the particular samples were available for testing.

Table 4-6 also shows the actual versus predicted performance of each catalyst, in the far right column. A value near 100% for this ratio indicates that the mercury oxidation reaction at the catalyst surface is nearly instantaneous, whereas a value less than 50% indicates a slower surface reaction. At high oxidation percentages this ratio becomes imprecise. Due to the exponential form of the calculation, NTU values become large as the oxidation percentage approaches 100%. Normal experimental error in quantifying performance at high oxidation percentages can make big differences in the observed NTU values, and can skew the actual versus predicted performance comparison.

Notwithstanding these potential errors, the comparison of actual to predicted NTU shows that even at the 3x palladium loading for Pd #1, virtually instantaneous oxidation at the catalyst surface was commonly measured (performance near 100% of the mass-transfer limit). Pd #1 at the 3x loading had measured performance that was 70% to over 100% of the mass-transfer limit, with the average for the six runs being right at 100% of the mass transfer limit. The SCR catalyst measured 57% to over 100% of the mass transfer limit, C#6 measured 37% to 51% of the mass transfer limit, and SBA #5 measured 30% to 76% of the mass transfer limit.

These percentages, when averaged over all runs for each catalyst type, suggest that Pd #1 was the most active catalyst tested, the SCR catalyst was the next most active, followed by SBA #5 and C#6. This ranking is not obvious in plots of performance versus area velocity in Figures 4-1 and 4-3, because the mass transfer model better takes into account the effects of differing catalyst geometry than does a simple area velocity calculation. Also, catalyst performance in simulated flue gas can be markedly different than its performance in an actual flue gas, as shown for SCR catalyst results later in this section.

The results shown in Table 4-6 were used to estimate the amount of each catalyst required to achieve high elemental mercury oxidation percentages in the pilot application. Table 4-7 shows the selected honeycomb dimensions for each catalyst and the overall catalyst dimensions required for the pilot unit as predicted by the mass transfer model described above. Note that the C #6 and SBA #5 catalysts were installed at a much lower area velocity than the Pd #1 catalyst, to account for their lower activity as measured in the laboratory tests described above.

The planned catalyst sizing was expected to be conservative, with area velocities in the range of 19 to 49 sft/hr [5.5 to 14 Nm/h]), and corresponding space velocities in the range of 5600 to 17,600 standard hr^{-1} (5300 to 16,700 Nh^{-1}). SCR catalysts installed for NO_X control on coal-fired units are typically designed for space velocities less than 5000 standard hr^{-1} (4700 Nh^{-1}) so for the most active, Pd #1 catalyst, the volume of catalyst tested represents much less than would be used for an SCR application.

Table 4-7
Catalyst Dimensions for the Laboratory Testing and Selected for the CCS Pilot Unit

Catalyst Type	Core Tested		Pilot Unit Catalyst					
	Cell Pitch (mm)	CPSI (cells per in^2)	Cell Pitch (mm)	CPSI (cells per in^2)	Catalyst Cross-section (in x in) [m x m]	Catalyst Length (in) [m]	Area Velocity (s ft/hr) [Nm/h]	Space Velocity (s hr^{-1}) [Nh^{-1}]
SCR	3.7	46	3.7	46	35.4 x 35.4 [0.90 x 0.90]	19.7 [0.50]	19 [5.5]	5600 [5300]
C #6	1.8	211	2.9	78*	36 x 36 [0.91 x 0.91]	9 [0.23]	28 [8.1]	12,200 [11,600]
SBA #5	1.7	217	2.9	78*	36 x 36 [0.91 x 0.91]	9 [0.23]	28 [8.1]	12,200 [11,600]
Pd #1	3.2	64	3.2	64	30 x 30 [0.76 x 0.76]	9 [0.23]	49 [14]	17,600 [16,700]

*Note – catalyst extrusion die was sized for 64 CPSI, but the catalysts shrunk to 78 CPSI on drying and firing

It was hoped that the field performance for these catalysts would be above 95% oxidation of elemental mercury at the design conditions shown in the table. However, as described later in this section, this did not prove to be the case for all of the catalysts.

Spruce Simulations

Laboratory testing of catalyst cores for mercury oxidation activity at simulated PRB (Spruce) flue gas conditions began in 2002. An initial list of candidate catalyst materials for the Spruce pilot was developed, based primarily on previous laboratory test results and initial results from the CCS pilot unit. Table 4-8 shows the list of catalysts considered. Candidate catalyst materials included the palladium-based material, an SCR-type catalyst (titanium/vanadium on alumina), an activated carbon/alumina monolith, and a fly-ash-based material. All four of these catalyst materials were being tested in the first pilot unit at CCS. A fifth, new material was also considered, gold on alumina. Gold has been patented by TVA for use as a flue gas elemental mercury oxidation catalyst.[8] Table 4-9 shows the laboratory gas compositions for the Spruce Plant simulations and compares that to the simulation gas for CCS conditions.

In laboratory catalyst screening tests run previously at CCS conditions, as discussed above, some scatter was seen in the results when testing Pd #1 catalyst cores. The scatter appears to have been caused by interference between some component in the sample gas exiting Pd #1 cores and the Tris solution used to remove oxidized mercury from the sample gas when measuring elemental mercury concentrations. This apparent interference caused a high degree of variability in the measured catalyst outlet elemental mercury concentrations, and thus caused some of the catalyst performance results to be suspect. Because of this apparent interference, the mercury analyzer operation was changed to use KCl solution rather than Tris solution to remove oxidized mercury.

Table 4-8
Catalyst Materials Considered for Evaluation in Pilot-scale Mercury Oxidation Tests

Catalyst Name (Abbreviation)	Description
Palladium #1 (Pd #1)	Commercial palladium catalyst wash coated on alumina substrate
SCR Catalyst (SCR)	Commercial NO_x catalyst; titanium-vanadium-based honeycomb
Carbon #6 (C #6)	Experimental activated carbon extruded in an alumina substrate
Subbituminous Fly Ash #5 (SBA #5)	Active fly ash extruded in an alumina substrate
Gold (Au)	Commercial gold catalyst wash coated on alumina substrate

Table 4-9
Comparison of Laboratory Simulation Gas Conditions for the Two Host Sites

Species	Spruce Conditions	CCS Conditions
SO_2 (ppm)	200	500
NO_x (ppm)	200	200
HCl (ppm)	2	6
O_2 (%)	5	5
CO_2 (%)	12	12
H_2O (%)	7	9
N_2 (%)	Balance	Balance
Temperature (^oF) [^oC]	300 [149]	350 [177]

Late in 2002, tests were conducted at simulated CCS conditions to compare the activity of gold as a catalyst to the activity of previously tested catalysts under similar conditions. It was determined that the KCl impinger solutions were being depleted very rapidly during these laboratory runs. The result of this depletion is a low bias in the indicated elemental mercury concentration. Thus, there was concern that the favorable results for the gold catalyst from 2002 were biased by depleted KCl impinger solutions. The cause of this apparent depletion remains unidentified.

Because of concern over depletion of the KCl impinger solutions, at the end of 2002 the laboratory run procedures were modified so the performance of each catalyst core was measured both with fresh Tris and fresh KCl solutions. Good agreement between results with the two impinger solution types was taken as an indicator that potential biases with each solution type were avoided. If the results with the two impinger solution types did not agree well, the test was repeated. All of the Spruce catalyst screening tests were conducted using this procedure.

Initial catalyst screening tests were conducted in late 2002, with samples of the Pd #1, SBA #5, and gold catalysts. Table 4-10 summarizes the results of those laboratory tests. However, as noted in the table, the gold results were considered suspect because of poor agreement between results measured with KCl and Tris impingers. As per the procedure described above, this meant that the gold tests would need to be repeated until better agreement was achieved.

Table 4-10
Spruce Laboratory Simulation Results (average results using KCl and Tris impingers for measuring elemental mercury concentrations)

Catalyst	Gas Flow Rate (l/min)	Inlet Hg^0 ($\mu g/Nm^3$)	Outlet Hg^0 ($\mu g/Nm^3$)	Hg^0 Oxidation (%)
Pd #1 3x; 1" core	0.94	31.1	2.88	91
Pd #1 3x; 1" core	1.3	21.7	2.61	88
Pd #1 3x; 1" core	1.7	15.9	1.75	89
SBA #5; 0.5" core	0.94	24.8	2.73	89
SBA #5; 0.5" core	1.3	18.9	2.63	81
SBA #5; 0.5" core	1.7	15.2	2.73	82
Au 1x; 1" core	0.94	34.0	0.94*	97*
Au 1x; 1" core	1.3	12.4	0.61*	95*
Au 1x; 1" core	1.7	9.48	1.30*	86*
Au 1x; 1" core, repeat	0.97	37.5	1.88	95
Au 1x; 1" core, repeat	1.3	27.5	3.58	87
Au 1x; 1" core, repeat	1.7	18.4	1.71	91
SCR catalyst; 1” core	0.94	31.0	5.37	83
SCR catalyst; 1" core	1.3	21.1	4.18	76
SCR catalyst; 1" core	1.7	16.1	4.38	77
C #6; 1" core	0.94	27.0	3.68	86
C #6; 1" core	1.3	19.6	3.97	80
C #6; 1" core	1.7	15.0	3.17	79

*Value is suspect because of poor agreement between Tris and KCl impinger results

In early 2003, the SCR and C #6 catalysts were evaluated and the gold was re-evaluated at Spruce conditions. These results are also shown in Table 4-10. This second set of gold catalyst tests confirms the high activity of the gold catalyst as was seen in the first set of results.

Figure 4-4 shows the results of all of the catalyst testing conducted in the laboratory at simulated Spruce conditions. Results from 2002 laboratory simulations for the Pd #1 and SBA #5 catalysts are plotted along with 2003 results for the gold, SCR and Carbon #6 catalysts.

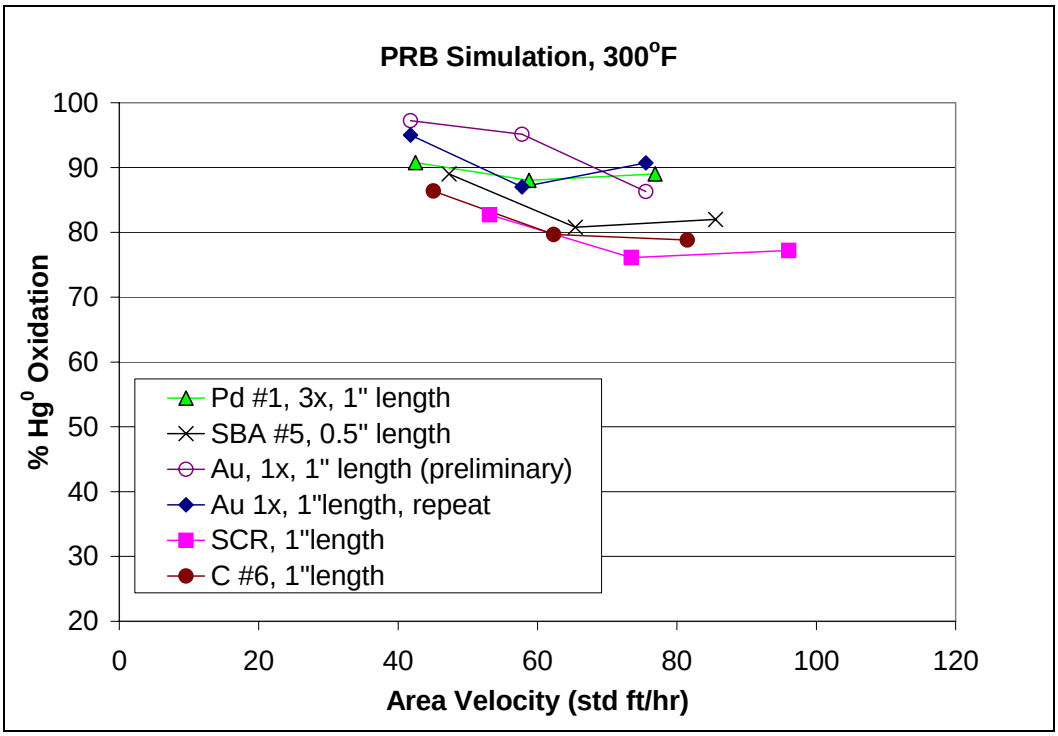

Figure 4-4
Effect of Area Velocity on Catalytic Oxidation of Hg^0 at Simulated Site 2 Conditions

When the results are plotted as a function of area velocity, the Pd and gold (Au) catalysts show the highest elemental mercury oxidation performance. Based on the high mercury oxidation percentage achieved with the gold catalyst in the laboratory, it was later decided that gold should be one of the four catalysts evaluated at Spruce Plant. The Pd #1 catalyst was also chosen to evaluate because of its high activity.

The SCR, SBA #5 and C #6 catalyst types showed lower, but similar performance for all three catalysts at the simulated PRB flue gas conditions. Since only two catalyst slots were available for testing at Spruce once the gold and Pd #1 catalysts were selected, it was decided to eliminate the SBA #5 catalyst and test the SCR and C #6 catalysts. The SBA #5 catalyst was eliminated because this catalyst type is produced from a single fly ash source and the raw material is available in only limited quantities, so it is of lesser interest for future commercial applications.

Catalyst Supply

For the CCS pilot unit, which was started up first, Argillon, Inc. (was Ceramics Gmbh, and Company, and previously Siemens) prepared a block of SCR catalyst based on the dimensions in Table 4-7. The completed catalyst block was shipped to CCS in late July 2002. Figure 4-5 shows a photograph of the completed catalyst block, ready for installation in the pilot unit.

Figure 4-5
Argillon Catalyst Block Ready for Installation in Pilot Unit

The Pd #1 catalyst for the CCS pilot unit was ordered from Sud-Chemie Prototech in the dimensions shown in Table 4-7. Prototech prepared the catalyst in three separate 3-in. (7.6-cm) deep catalyst blocks. These three blocks were shipped to the CCS site in September 2002.

The C#6 and SBA #5 catalysts were custom-prepared by a U.S.-based catalyst manufacturer who does not wish to be identified. These catalysts were prepared as extruded monoliths with a ceramic substrate. Since this is the first time that either of these materials has been processed into a honeycomb form, the manufacturer had to conduct a considerable amount of development work to determine mixing, extruding, drying and firing parameters. Although the catalyst samples prepared for the simulated flue gas investigations described above were prepared by the manufacturer in their laboratory, commercial equipment was used for preparing catalyst quantities for the pilot unit. Consequently, these experimental efforts had to be scheduled between commercial catalyst production runs.

The vendor first conducted an experimental extrusion of the SBA #5 catalyst, as a preparation for the “production” run to prepare enough material for the pilot unit. Figure 4-6 is a photograph of a

sample 5.9-in. by 5.9-in. by 3-in. (15-cm by 15-cm by 7.6-cm) deep catalyst block of the SBA #5 test extrusion.

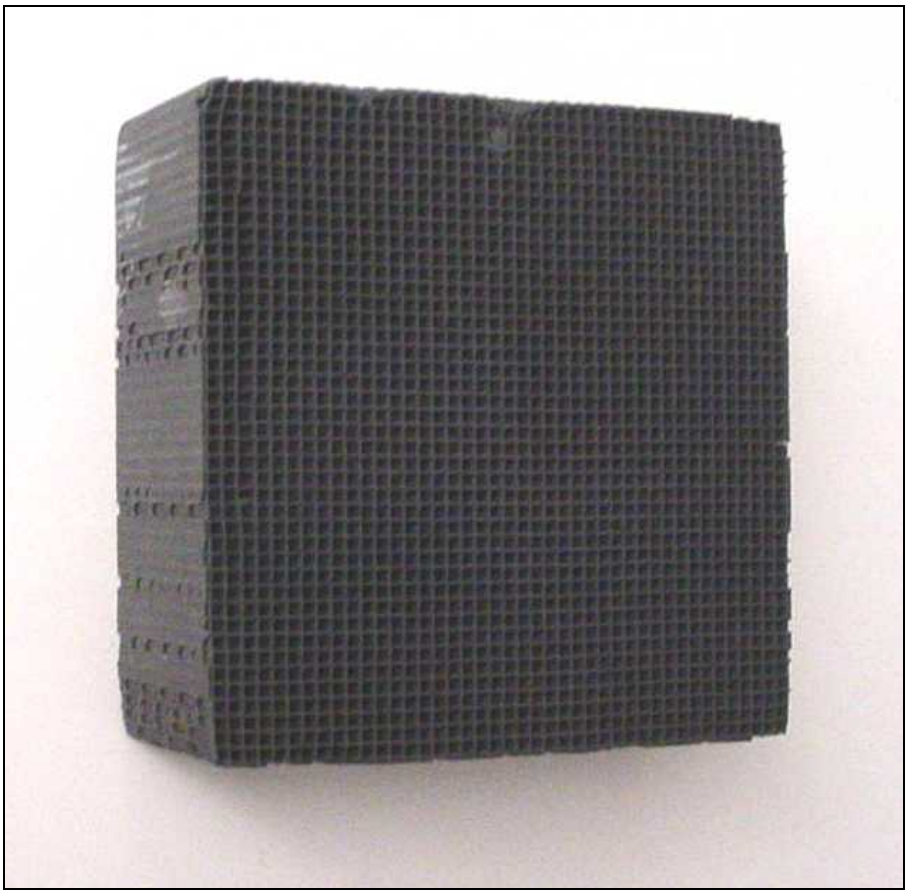

Figure 4-6
Sample Catalyst Block for SBA #5, as Prepared by Catalyst Manufacturer

The “production” extrusion of the pilot unit SBA #5 catalyst blocks was completed at the end of September 2002. During October, these catalyst blocks were dried and fired, and in November 2002 they were “canned” into metal containers of appropriate dimensions for the pilot unit. “Canning” involves stacking the 5.9-in. (15-cm) square catalyst blocks into an array of the desired cross-sectional area (six by six blocks in this case) in a steel enclosure that holds them together. The front and rear faces of the enclosure were covered with steel mesh that allows flue gas flow but prevents the catalyst blocks from being displaced.

Figure 4-7 shows an overall view of one of the three SBA #5 catalyst cans that were installed in the pilot unit in December. Figure 4-8 is a close-up shot of the same can, which shows how individual 5.9-in. by 5.9-in. (15-cm by 15-cm) blocks were stacked to produce the nominally 36-in. by 36-in. (0.9-m by 0.9-m) cross section.

Figure 4-7
Photograph of One of Three SBA #5 Catalyst Cans

Figure 4-8
Close-up of One of Three SBA #5 Catalyst Cans

In December 2002, the preparation of the C #6 catalyst began. A 300-lb (140-kg) lot of activated C #6 material, prepared by the Illinois State Geological Survey and MaxWell Engineering and Consulting, was ground to size for extrusion. The C #6 catalyst was custom-prepared by the same U.S.-based catalyst vendor that prepared the SBA #5, as extruded monoliths in a ceramic substrate. The extrusion, drying, firing and canning of these catalyst blocks was completed during the first quarter of 2003, and the completed catalysts were received by URS at the end of March 2003.

The C #6 catalyst cans had spacers added to center them in the pilot unit catalyst chamber and to ensure a tight fit against the chamber walls to miminize gas sneakage. The modified catalyst cans were shipped to CCS but were not installed in the pilot unit until early June 2003. The installation was delayed pending the results of efforts to retrofit on-line catalyst cleaning on the pilot unit to control the buildup of fly ash on the horizontal catalyst surfaces. This is further discussed in the following subsection.

The startup of the second pilot unit at Spruce Plant lagged the CCS startup by approximately 11 months. In early July 2003, the catalyst dimensions for the pilot unit at Spruce Plant were determined based on the laboratory results described above and CCS activity results, and all four catalysts were ordered from their respective suppliers. This decision was made as late in the year

as possible, so as to benefit from interim results from the first pilot unit at CCS. In particular, the results of efforts to minimize fly ash buildup in the horizontal gas flow catalyst modules, and initial activity results for the C #6 catalyst in actual flue gas (measured in June 2003) were needed to support catalyst selection and sizing decisions.

Table 4-11 summarizes the catalyst dimensions. Because of tendencies for fly ash to build up in the horizontal-gas-flow honeycomb cells of the catalysts, some consideration was given to ordering catalysts with larger cell sizes (fewer cells per square inch) to reduce fly ash buildup. However, because Spruce Plant has a baghouse rather than an ESP for primary particulate control, it was expected that the fly ash loading at the pilot unit inlet would be lower than at CCS, and would have less of a residual electrostatic charge. For these reasons, results for fly ash accumulation with larger catalyst cells at Spruce would not likely predict catalyst performance at a plant with an ESP. Therefore, it was decided to stay with the same catalyst dimensions as was being tested at CCS, so performance results from the two sites would be directly comparable. The one exception was the SCR catalyst, which was tested at a greater catalyst length at Spruce because of its relatively low elemental mercury oxidation activity at CCS.

Table 4-11
Catalyst Dimensions for Oxidation Catalyst Pilot Unit at Spruce Plant

Catalyst	Cells per in.^{2} (cpsi) [cells/cm^2]	Cross Section (in. x in.) [cm x cm]	Length (in.) [cm]	Area Velocity (sft/hr) [Nm/h]
Pd #1	64 [9.9]	29.5 x 29.5 [75 x 75]	9 [23]	49 [14]
Au	64 [9.9]	29.5 x 29.5 [75 x 75]	9 [23]	49 [14]
C #6	80* [12]	35.4 x 35.4 [90 x 90]	9 [23]	27 [7.7]
SCR	46 [7.1]	35.4 x 35.4 [90 x 90]	29.5 [75]	13 [3.7]

*Die is sized at 64 cpsi, but shrinkage to this pitch occurs on drying

The Pd #1 and Au catalysts were ordered from Süd-Chemie Prototech and delivered to Spruce Plant in August, 2003. The Argillon SCR catalyst was not delivered at Spruce Plant until September 29, due to the Argillon production facilities shutting down in August for summer vacation.

The C #6 catalyst took the longest time to procure because of the multiple process steps by several subcontractors that have to take place to produce this material in honeycomb catalyst form. The raw carbon feedstock had to be procured, activated, and ground to size. Then, as described earlier for the CCS catalyst, the catalyst maker had to slurry the material with a ceramic substrate, extrude, dry, fire, and can the catalyst blocks. The C #6 catalysts were delivered to Spruce Plant in late October and installed in the pilot unit on November 13, 2003.

Pilot Test Program Results

CCS Results

Initial Pilot Unit Operation

The CCS pilot unit was started up with no catalysts loaded during the week of September 16, 2002. The no-catalyst startup was conducted to ensure that desired flue gas flow rates could be attained, and that flue gas temperature, flow rate, and pressure instrumentation and controls worked properly. The pilot unit data acquisition system and telemetry equipment was also checked for proper functionality.

The start up went well. Pilot unit flow rates were readily controlled at 2000 acfm (3400 m^3/hr) per compartment (although with no catalysts installed to add pressure drop) and pilot unit flue gas temperatures could be controlled above 300^{o}F (150^{o}C) even before the inlet ductwork insulation was complete. No flue gas leaks of any significance were observed, and no problems were encountered dialing up the pilot unit's data acquisition system from off site and downloading process data files. The pilot unit was left operating with no catalysts until the planned loading of the SCR and Pd #1 catalysts the first week of October. As described previously in this section, the other two catalysts (SBA #5 and C #6) were not yet available, so a decision was made to commence testing with only two of the four catalysts installed.

The SCR and Pd #1 catalysts were placed in flue gas service at 2000 acfm (3400 m^3/hr) through each catalyst the evening of October 3. It was expected that these new catalysts would have a significant capacity for adsorbing mercury from the flue gas, so no catalyst performance measurements were made at that time. With mercury being adsorbed from the flue gas, it is not possible to get an accurate measurement of elemental mercury oxidation. The percent oxidation across the catalyst is based on the drop in elemental mercury across the catalysts, and with mercury being adsorbed it is not possible to distinguish between the drop in concentration due to adsorption and that from oxidization.

The catalysts were left in service until the week of October 14, when initial catalyst activity measurements were made using the EPRI Hg SCEM. The Hg SCEM was previously described in Section 3. The two catalysts were measured for mercury oxidation percentage at three different flue gas flow rates. The results of these measurements are summarized in Table 4-12. A second catalyst activity measurement trip was made the first week of December. The results from that trip are summarized in Table 4-13.

In these tables, and throughout this report, the elemental mercury oxidation percentages across the catalysts are based on the change in elemental mercury concentration across the catalyst, and do not just reflect the total flue gas mercury oxidation percentage at the catalyst outlet.

Table 4-12
October 2002 Catalyst Activity Results (Hg concentrations reported as measured, uncorrected for sample gas O_2 content)

Flue Gas Rate (acfm) [m^3/hr]	Inlet Total Hg ($\mu g/Nm^3$)	Inlet Hg^0 ($\mu g/Nm^3$)	Inlet Hg Oxidation (%)	Pd #1 Results			SCR Catalyst Results		
				Catalyst Outlet Hg^0 ($\mu g/Nm^3$)	Catalyst Hg^0 Oxidation (%)	Catalyst Area Velocity (sft/hr) [Nm/h]	Catalyst Outlet Hg^0 ($\mu g/Nm^3$)	Catalyst Hg^0 Oxidation (%)	Catalyst Area Velocity (sft/hr) [Nm/h]
1500 [2550]	8.3	4.6	43	0.25	95	37 [11]	1.5	67	14* [4.0]
2000 [3400]	10.8	7.4	32	0.52	93	49* [14]	2.8	62	19 [5.5]
2300 [3900]	8.0	4.7	42	0.50	89	56 [16]	1.8	61	22 [6.3]

Note: 1.0 $\mu g/Nm^3$ ~ 0.8 lb Hg per 10^{12} Btu heat input
*Conditions selected for long-term catalyst operation

Table 4-13
December 2002 Catalyst Activity Results (Hg concentrations reported as measured, uncorrected for sample gas O_2 content)

Flue Gas Rate (acfm) [m^3/hr]	Inlet Total Hg* ($\mu g/Nm^3$)	Inlet Hg^0* ($\mu g/Nm^3$)	Inlet Hg Oxidation* (%)	Pd #1 Results			SCR Catalyst Results		
				Catalyst Outlet Hg^0 ($\mu g/Nm^3$)	Catalyst Hg^0 Oxidation (%)	Catalyst Area Velocity (sft/hr) [Nm/h]	Catalyst Outlet Hg^0 ($\mu g/Nm^3$)	Catalyst Hg^0 Oxidation (%)	Catalyst Area Velocity (sft/hr) [Nm/h]
1000 [1700]	- /14.3	- /9.1	- /36	-	-	-	6.4	30	10 [2.9]
1500 [2550]	14.3/17.7	9.1/8.8	36/50	3.0	67	37 [11]	6.3	28	14** [4.0]
2000 [3400]	17.7/16.7	8.8/8.8	50/47	4.1	53	49** [14]	7.0	21	19 [5.5]
2200 [3750]	16.7/ -	8.8/ -	47/ -	3.7	58	54 [16]	-	-	-

Note: 1.0 $\mu g/Nm^3$ ~ 0.8 lb Hg per 10^{12} Btu heat input
*First value listed is the inlet condition for the Pd #1 catalyst, second value is for the SCR catalyst
**Denotes normal operating condition for catalyst

The October results showed high activity for the Pd#1 catalyst, very near that expected based on previous laboratory and field testing with this material. The SCR catalyst results showed significantly lower oxidation percentages at the same flue gas flow rates, and lower oxidation performance than had been expected.

Figure 4-9 plots these activity results. In the figure, the October oxidation percentage results for the two catalysts are plotted as a function of area velocity. Projected performance of the catalysts based on results of previous laboratory tests is also plotted.

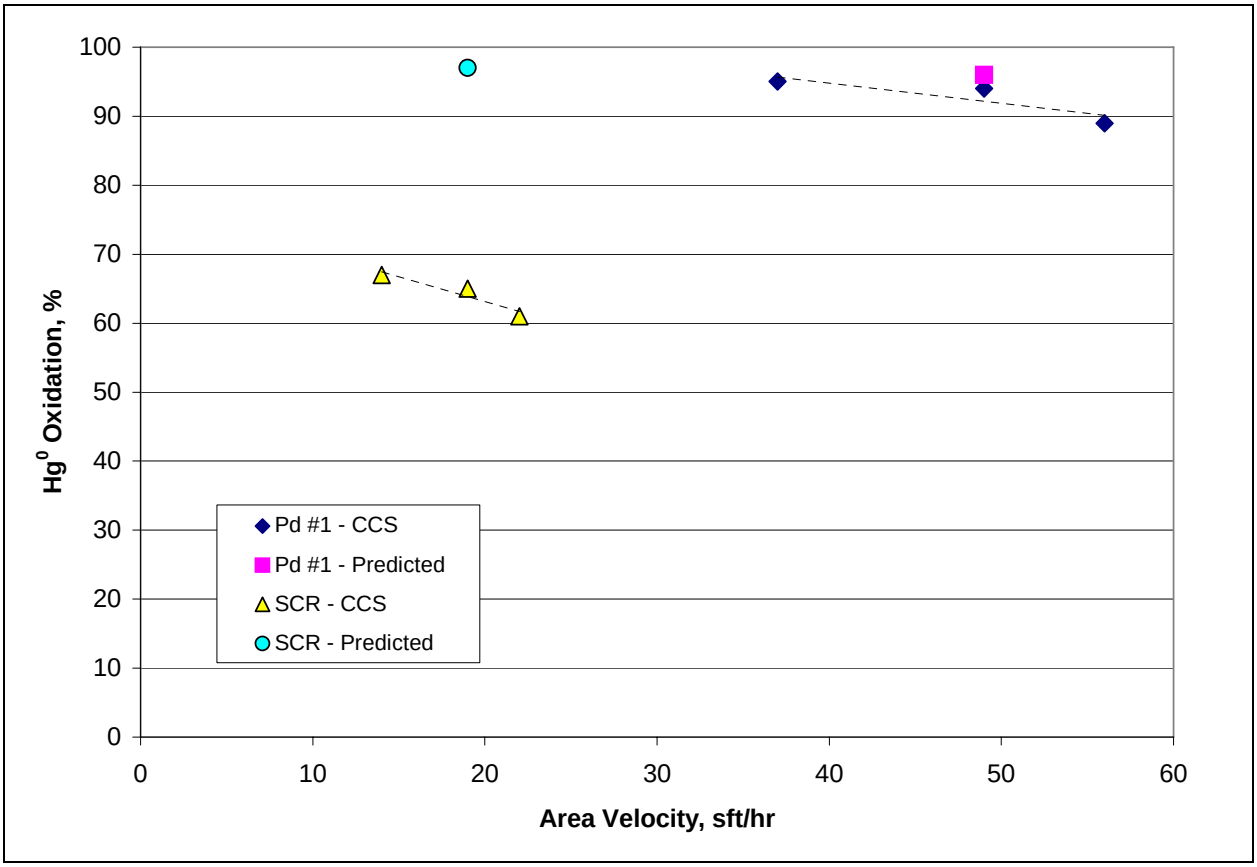

Figure 4-9
Predicted vs. Actual Elemental Mercury Oxidation across Catalysts at CCS, October 2002

The December results summarized in Table 4-13 showed a marked decrease in activity for both catalysts. The percentage oxidation of elemental mercury across the Pd #1 dropped from greater than 90% in October to approximately 50 to 70% in December. The elemental mercury oxidation across the SCR catalyst dropped from 60 to 70% in October to 20 to 30% in December.

Figure 4-10 plots the catalyst activity data as a function of catalyst time in flue gas service, for operation of each catalyst at a flue gas flow rate of 1500 acfm [2550 m^3/hr]. This corresponds with an area velocity of 37 sft/hr (11 Nm/h) for Pd #1 and 14 sft/hr (4.0 Nm/h) for the SCR catalyst. The data for Pd #1 at its normal flue gas flow rate of 2000 acfm [3400 m^3/hr] data were

not plotted in this figure because the December data for that flow rate appear to be anomalous, showing a lower oxidation percentage than was measured at the higher flue gas rate.

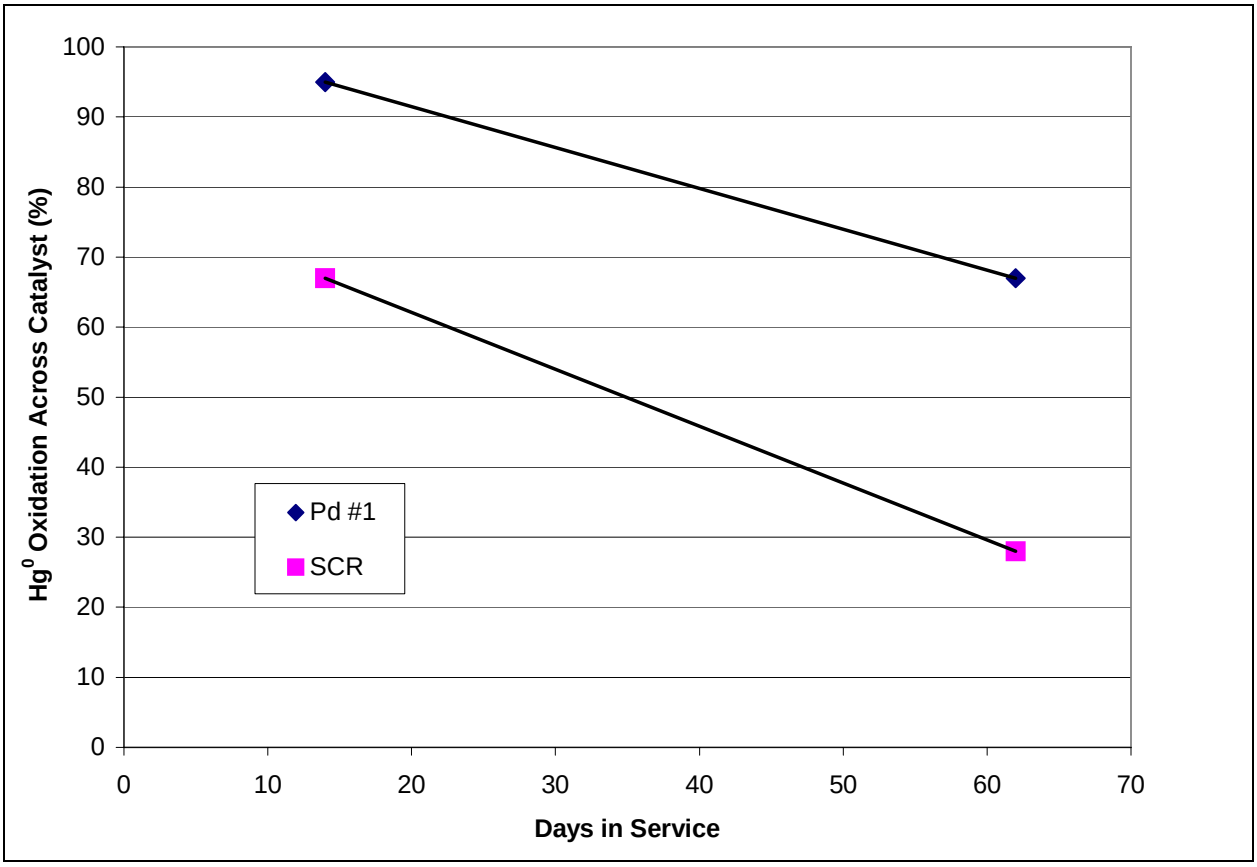

Figure 4-10
Apparent Loss of Activity versus Time in Service at CCS at 1500 acfm (2550 m^3/hr) Flue Gas Flow Rate

Several possible explanations for this apparent loss of activity were considered, including:

- The catalyst outlet elemental mercury concentration data from December could be biased high due to an undetected measurement problem, although this did not seem likely given the normal appearing inlet values.

- The catalyst surfaces may be becoming fouled due to a buildup of fly ash, in spite of the catalyst being installed downstream of a high-efficiency ESP.

- Some species in the lignite-fueled flue gas at CCS may be causing rapid loss of catalyst activity.

It seemed likely that the second explanation was the cause of the apparent activity loss. At the measured particulate loading of 0.004 gr/dscf in the pilot unit inlet gas, approximately 60 lbs (27 kg) of fly ash would have passed through the Pd #1 catalyst at 2000 acfm (3400 m^3/hr) over 62

days. If a significant percentage of that fly ash accumulated within the catalyst chamber and/or on the honeycomb surfaces, this could account for the observed loss of apparent activity.

Further evidence of fly ash buildup was seen in the measured pressure drop across the catalyst chambers. When the two catalysts were put into service in October, the initial clean catalyst pressure drop across each chamber was about 0.25 in. H_2O (0.1 kPa). By the end of December 2002, the indicated pressure drop across the chambers had steadily increased to about 1.5 in. H_2O (0.38 kPa) across the SCR catalyst and over 3 in. H_2O (0.75 kPa) across the Pd #1 catalyst. The differential pressure transducers were, at the time, scaled for readings of 0 to 3 in. H_2O (0 to 0.75 kPa). The third catalyst, SBA #5, also showed a dramatic increase in pressure drop over time since it was placed in service in early December 2002.

Figure 4-11 shows pressure drop versus time for all four catalyst chambers (including the empty chamber) from the beginning of October 2002 through mid-January 2003. As mentioned above, since the pilot unit instrumentation was scaled to read a maximum of 3 in. H_2O differential (0.75 kPa), the pressure-drop data for the SBA #5 and Pd #1 catalysts became pegged at full scale.

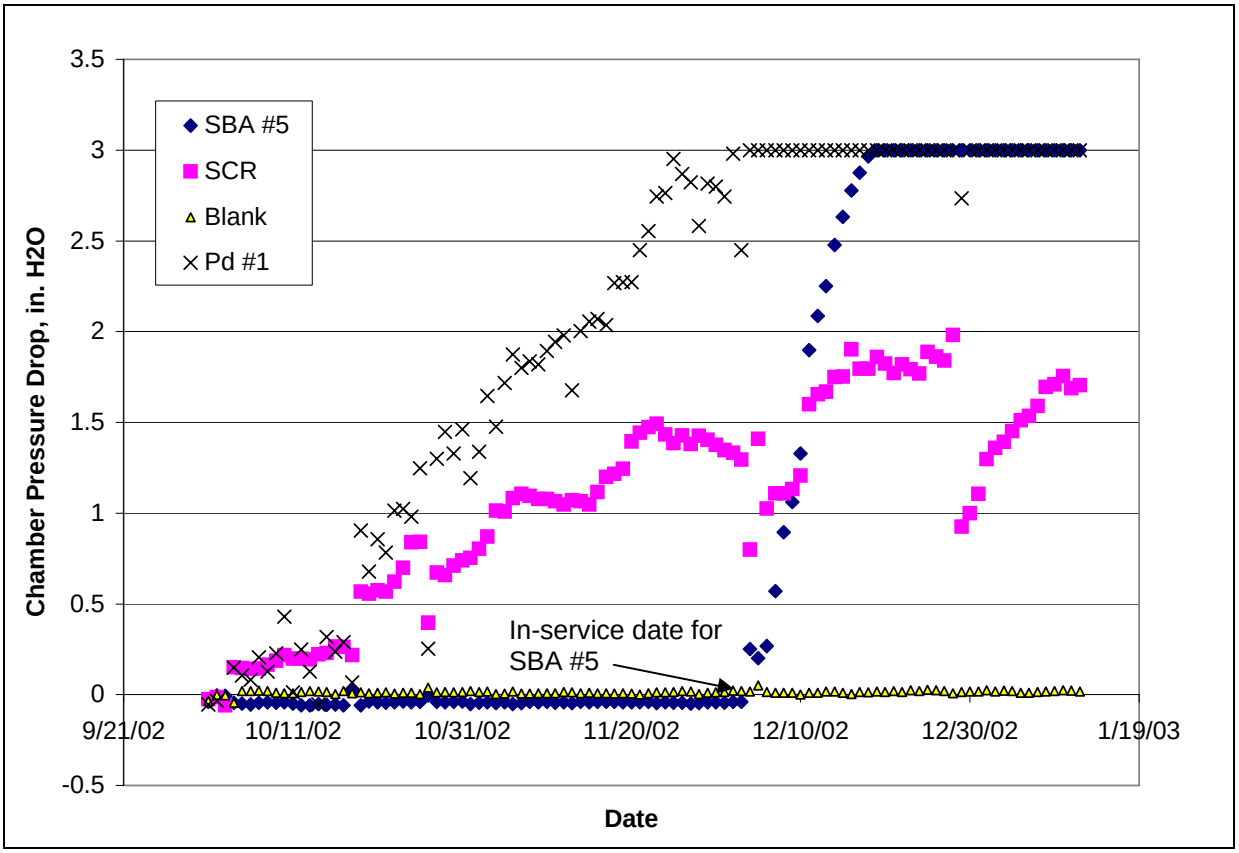

Figure 4-11
Catalyst Chamber Pressure Drop versus Time in Service

The next catalyst activity measurement trip occurred the week of January 20, 2003. The objective of that trip was to determine whether the apparent loss of activity continued with time, stabilized, or had reversed (i.e., improved activity compared to December results). Also, the

catalyst pressure-drop indications by the pilot unit instrumentation were verified and the instruments were re-scaled to read higher differential pressures (0 to 10 in. H_2O differential [0 to 2.5 kPa]). The plan was that, if the activities of the catalysts were still well below the October values, and if the high pressure-drop values were confirmed, the catalyst chambers would be opened to observe whether there was significant fly ash buildup. If so, an attempt would be made to clean the catalyst surfaces with a vacuum cleaner and dry compressed air.

The January trip also provided the first opportunity to measure the activity of the SBA #5 catalyst. However, it was expected that it too would be adversely affected by fly ash buildup, based on the observed pressure differential readings.

The January results did confirm elevated pressure-drop readings across the catalyst modules, and showed lower catalyst activity for the SCR catalyst and Pd #1 than in October. Based on these results, the catalyst modules were shut down and opened for inspection. Each was found to have significant fly ash build up.

Figures 4-12 and 4-13 are photographs that show the surface of the Pd #1 catalyst before and after the cleanup. Although the buildup was extensive, the fly ash remained dry and free flowing and was readily removed.

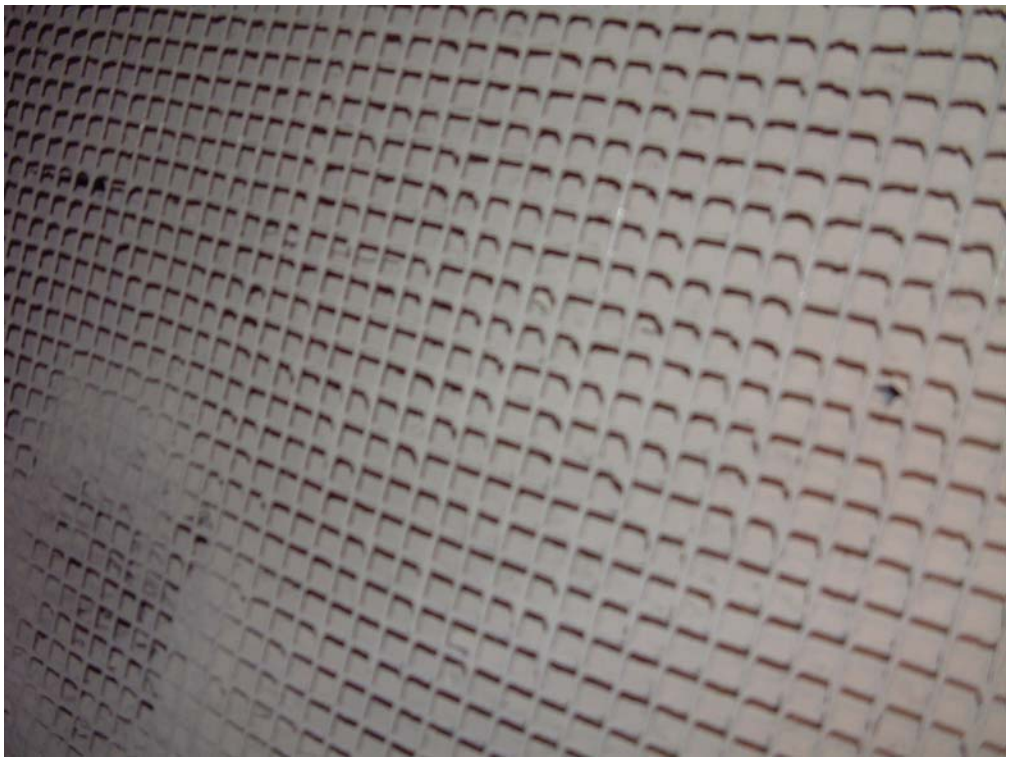

Figure 4-12
Photograph Depicting Fly Ash Buildup on the Pd #1 Catalyst Surface in January 2003

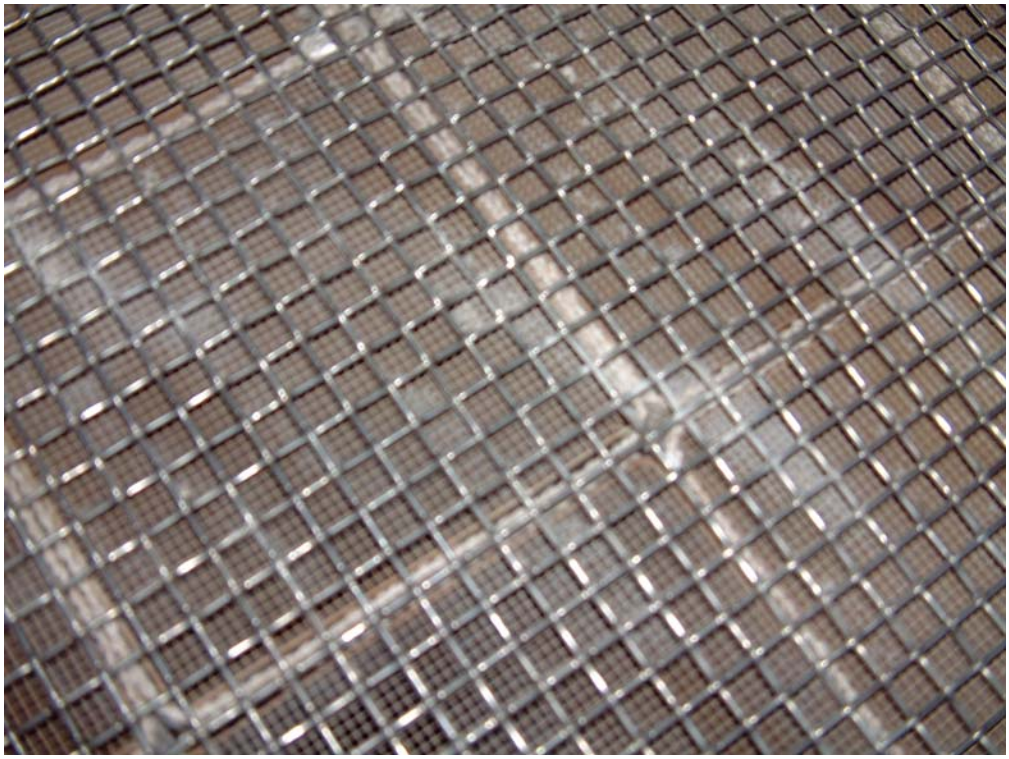

Figure 4-13
Photograph Depicting the Surface of the Pd #1 Catalyst after Clean-up in January 2003

The modules were cleaned by vacuuming loose fly ash, and using compressed air to dislodge fly ash collected within the honeycomb passages. After cleaning all three catalyst-containing chambers, the pilot unit was put back in service.

Physically cleaning the catalysts of fly ash buildup appeared to have restored nearly all of their original activity. The catalyst activity results from before and after the January cleaning are shown in Table 4-14. For comparison, results from the previous October and December measurement trips are also shown.

Note in the table that the January 22, "as found" values were equal to or actually a little better than the December measurements, which suggests the catalysts had reached some sort of steady state blockage of catalyst surface area. Also note that the fly-ash-based catalyst was not as active as had been hoped (75% oxidation after cleaning), although it might have been a little higher had measurement results been available when it first went into service.

Table 4-14
Summary of the First Six Months of Hg^0 Oxidation Catalyst Activity Results at CCS

Catalyst (Flow Rate, acfm)	Hg^0 Oxidation across Catalyst (%)					
	October 17	December 3	January 22	January 24 (after cleaning)	March 27 (prior to cleaning)	March 27 (after cleaning)
SBA #5 (2000)	NA*	NA	59	75	14	NA
SCR (1500)	67	28	37	61	4	NA
Pd #1 (2000)	93	53	58	91	NA	92

*NA - No measurement results available for these dates

CCS Long-term Catalyst Pressure-drop Results

Based on these results, it was decided that some method of mechanical cleaning should be implemented on the pilot unit. Both air soot blowers and sonic horns were considered. After reviewing full-scale SCR experiences with on-line catalyst cleaning and talking to a number of soot blower and sonic horn vendors, it was decided that a sonic horn retrofit would be the easiest field retrofit at CCS and would have a good probability of success. A small, 17-inch (0.43-m) horn produced by Analytec Corporation of Pagosa Springs, Colorado was selected based on price, availability, and probability of success.

During the last week of March 2003, another site visit was made to CCS to install the sonic horn on the Pd #1 catalyst box and to measure the oxidation of mercury across each of the three installed catalysts. The sonic horn was to provide occasional pulses of acoustic energy to the catalysts to dislodge accumulated particulate matter. It was installed on the top wall of the catalyst housing inlet transition, approximately 1.5 feet (0.5 m) upstream of the first catalyst module. The horn was supplied compressed air by a dedicated plant air line, and programmed to sound for 10 seconds every half hour.

The catalyst housing was opened during the horn installation, allowing an opportunity to clean the Pd #1 catalyst modules. All three of the Pd #1 modules were coated with a thick layer of particulate matter as they had been in January. The modules were cleaned with compressed air and a vacuum as before.

The other two catalyst chambers were not cleaned during this trip. Once the Pd #1 catalyst modules were cleaned and the horn was installed, flue gas flow was resumed. Mercury oxidation measurements were made for each of the three installed catalysts. The SBA #5 catalyst oxidized only 14% of the inlet elemental mercury and the SCR catalyst oxidized 4% of the inlet elemental mercury. As mentioned above, neither the SBA #5 nor the SCR catalysts were cleaned. The cleaned Pd #1 catalyst oxidized 92% of the inlet elemental mercury, so, as in January, physically cleaning the fly ash from the catalyst restored its activity. These March results were also included in Table 4-14 above.

The plan was that, if effective, a horn would be installed on each of the other catalyst chambers. Figure 4-14 illustrates the pilot unit pressure-drop data for all three catalysts from October 2002 (December 2002 for the SBA #5 catalyst) through May 27, 2003. The horn was clearly effective at controlling the pressure drop across the Pd #1 catalyst.

The data for Pd #1 (the lightest shaded line on the figure) show the pressure drop pegged at over 3 in. H_2O (0.74 kPa) from early December 2002 through late January 2003, when the pressure differential transducers were recalibrated to measure up to a 10-in.-H_2O (2.5-kPa) differential. The differential across the Pd #1 chamber was then measured at 5 to 6 in. H_2O (1.2 to 1.5 kPa). After the catalyst was cleaned and the pilot unit was put back into service, the signal from the pressure differential transducer on the Pd #1 catalyst was producing a noisy signal. This was likely due to moisture condensation in the tubing to the pressure-drop transducer for this compartment during winter operation.

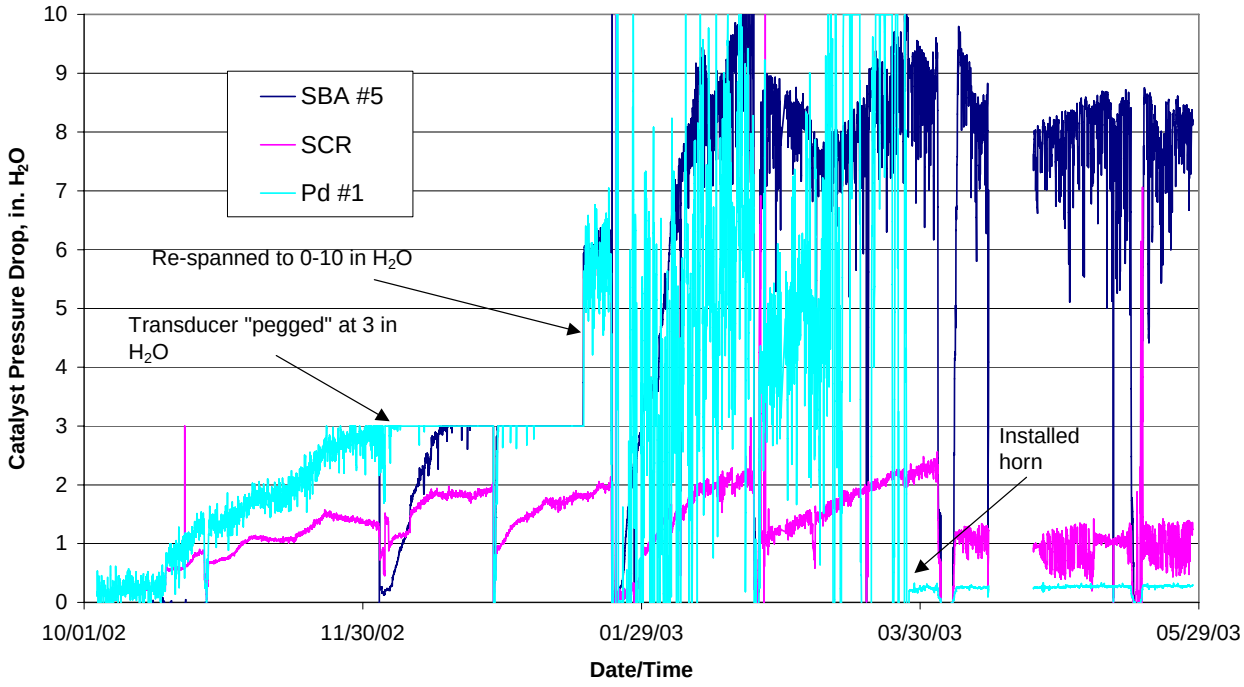

Figure 4-14
Pressure-drop Data for the Three Catalysts in Service at CCS through May 27

Note: 1 in. H_2O = 0.25 kPa

On average, the pressure drop across the Pd #1 catalyst increased to 6 or 7 in. H_2O (1.5 to 1.7 kPa) within three weeks after the catalyst was cleaned. After a host unit trip the pressure drop was reduced to about 4 to 5 in. H_2O (1.0 to 1.2 kPa), then increased again until the pilot unit was brought off line in late March to install the sonic horn. During the following two months, between when the horn was installed and May 27, the pressure drop across the Pd #1 catalyst increased by only 0.1 in. H_2O (0.02 kPa), ending at 0.3 in. H_2O (0.07 kPa).

The true measure of the effectiveness of the horn would be if the Pd #1 catalyst also retained high activity. A catalyst activity measurement trip was conducted the week of April 23 to provide this information. When the samplers arrived the morning of April 23, the pilot unit was found off-line due to a station power outage on April 13. The unit did not restart when power was restored, as was intended, apparently due to a problem with an "uninterruptible power supply" (UPS) used as a power conditioner for the pilot unit control computer. The power outage was long enough to run down the battery backup in the UPS, and the UPS did not reset automatically after power was restored. The pilot unit was restarted on April 23 and ran overnight while total mercury concentrations were measured at the outlet of each catalyst. On April 24, the oxidation performance was measured for the three installed catalysts. The results of these measurements are summarized in Table 4-15.

Table 4-15
Summary of Catalyst Activity Results from CCS, April 2003 (Hg concentrations reported as measured, uncorrected for sample gas O_2 content)

Flue Gas Sample	Total Hg Concen-tration ($\mu g/Nm^3$)*	Elemental Hg Concen-tration ($\mu g/Nm^3$)	Overall Hg Oxidation (% of total)*	Observed Hg Adsorption across Catalyst (%)	Hg^0 Oxidation across Catalyst (%)	Flue Gas Flow Rate (acfm) [m^3/hr]	Catalyst Area Velocity (sft/hr) [Nm/h]
Inlet to Pilot Unit	18.6	8.92	52	NA**	NA	NA	NA
SBA #5 Out	18.7	8.04	57	0	10	2000 [3400]	33 [9.4]
SCR Out	18.4	7.89	57	1	12	1500 [2550]	14 [4.0]
Pd #1 Out	9.45	1.01	89	49	89	2000 [3400]	49 [14]

* Note: 1.0 $\mu g/Nm^3$ ~ 0.8 lb Hg per 10^{12} Btu heat input
**NA – not applicable

After being off line for over a week, the Pd #1 catalyst appeared to have renewed mercury adsorption capacity – the catalyst outlet total mercury concentration was about half of the inlet value. Oxygen concentration measurements on the sample gas from the Pd #1 outlet showed normal O_2 levels, so there was no indication of a leak in the sample from that box. Such a leak could have introduced a low bias in the outlet total mercury measurements. The SCR catalyst and SBA #5 catalyst were not adsorbing any mercury according to these results.

Activity results showed that the Pd #1 catalyst, after being kept clean with the sonic horn, was achieving nearly 90% oxidation of elemental mercury while the "dirty" SCR and SBA #5 catalysts were relatively inactive (10-12% elemental mercury oxidation). However, the Pd #1 results were confounded by the apparent mercury adsorption (i.e., some of the drop in elemental mercury concentration across the Pd #1 could be due to adsorption rather than oxidation).

In spite of this confounding effect, the Pd #1 results were taken to be quite encouraging. Based on the relatively high activity and low pressure-drop values for Pd #1, efforts to install similar Analytec sonic horns on the other three boxes were begun. It was also planned that the fourth catalyst (C #6) would be installed at the same time as the sonic horn installation. Since the sonic horn should prevent fly ash buildup, it was expected that catalyst would be able to avoid any operation with substantial fly ash plugging or fouling.

The other three sonic horns were installed by CCS personnel the first week of June. On June 2, the pilot unit was again found to be off line, this time apparently due to a station power outage the evening of May 27. After two such occurrences within a period of two months, the problematic UPS was replaced.

The catalyst chambers were opened on June 2nd and 3rd without first restoring flue gas flow, and fly ash buildup was cleaned out with compressed air. For the Pd #1 catalyst, none of the catalyst cells appeared to be plugged, but a small amount of fly ash was observed to blow out of each cell when it was cleaned. The fly ash buildup was more substantial in the SCR catalyst, where it appeared that a circle of cells about 18 inches (46-cm) in diameter was all that remained open for flue gas flow; all of the outboard cells appeared to be plugged with fly ash. The fly ash was relatively dry and free flowing, and the SCR catalyst was readily cleaned out.

On the SBA #5 catalyst, the fly ash buildup was more substantial and appeared to be more tenacious. It was not clear how flue gas was flowing through the SBA #5, as virtually all of the cells on the front face of the first catalyst layer appeared to be plugged. The ash seemed to have been partially “set up,” and it took more effort to blow the fly ash deposits loose with compressed air than was required with the SCR catalyst. This apparent setting up may have been a result of the pilot unit being off line for several days prior. The catalyst chambers cooled while still full of moist flue gas because of the unplanned power outage.

Not all of the plugged catalyst cell openings on the first layer of the SBA #5 catalyst could be cleaned with compressed air. Some buildups were too tenacious, so the plugs were left in place. It was estimated that approximately 2% of the cells in the first catalyst layer were left plugged. Also, the screens that hold the catalyst blocks in place in the catalyst “cans” had become bowed over time. This bowing reduced the clearance between catalyst layers, which made it difficult to get the compressed air probe in position to clean all of the cells in the second and third layers. The buildup in the second and third layers appeared to be much more dry and free flowing than on the face of the first layer, though.

The horns were installed on the other three compartments (the initial horn remained on the Pd #1 compartment), and the fourth catalyst (C #6) was installed. Figure 4-15 shows a typical sonic horn installation on a catalyst chamber inlet transition duct.

Figure 4-15
Typical Sonic Horn Installation on the Pilot Unit at CCS

The pilot unit was restarted on June 5 with all four catalysts installed and the sonic horns in service on each compartment (10 seconds each every 30 minutes). With the horns in service, the pressure drops across three of the four catalysts stayed low. The pressure-drop values from June 5,2003 through early January 2004 are plotted in Figure 4-16.

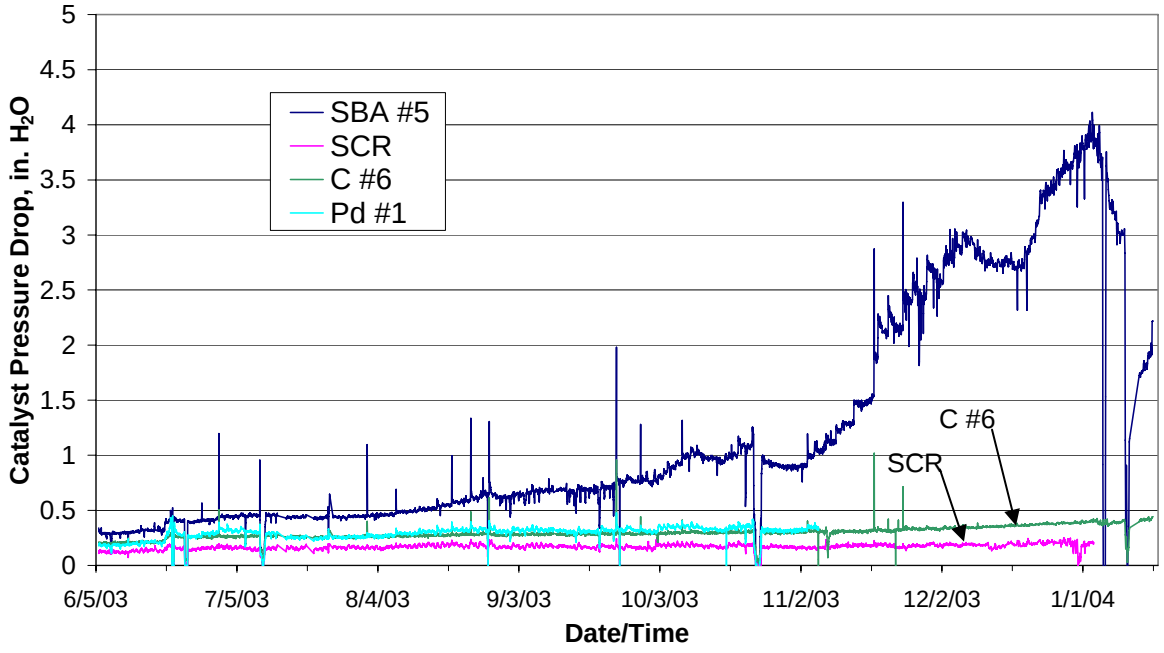

Figure 4-16
Pressure-Drop Data for the Catalysts in Service at CCS, June through early January 2004
Note: 1 in. H_2O = 0.25 kPa.

By the early January 2004, the C #6 pressure drop was about 0.4 in. H_2O [0.1 kPa], and the SCR catalyst (larger pitch and 1500 acfm [2550 m^3/hr] flow rate) pressure drop was about 0.2 in. H_2O [0.05 kPa]. The pressure drop across the Pd #1 catalyst was virtually identical to that across the C #6 until November 5, when the Pd #1 signal became noisy. The data after November 5 were edited from the figure. The same thing happened with this transducer during cold weather operation the previous winter, as noted above. The last "good" data points on November 5 showed that the pressure drop across this catalyst remained low at 0.35 in. H_2O [0.09 kPa]. The SBA #5 pressure drop continued to increase with time, to nearly 4 in. H_2O [1 kPa] by the end of December, more than 10 times the initial pressure drop on June 5.

Pressure-drop values from June 5, 2003 through the end of the long-term test in June 2004 are plotted for the Pd #1 and SBA #5 catalysts in Figure 4-17. If all four catalyst pressure-drop values were plotted, the plot would become indecipherable due to the noisy signals. However, the data from nearly 13 months of operation plotted in Figure 4-17 illustrate the difference in performance between the one catalyst that was not effectively kept clean by the sonic horn (SBA #5) and the other three that were (as illustrated by the Pd #1 data).

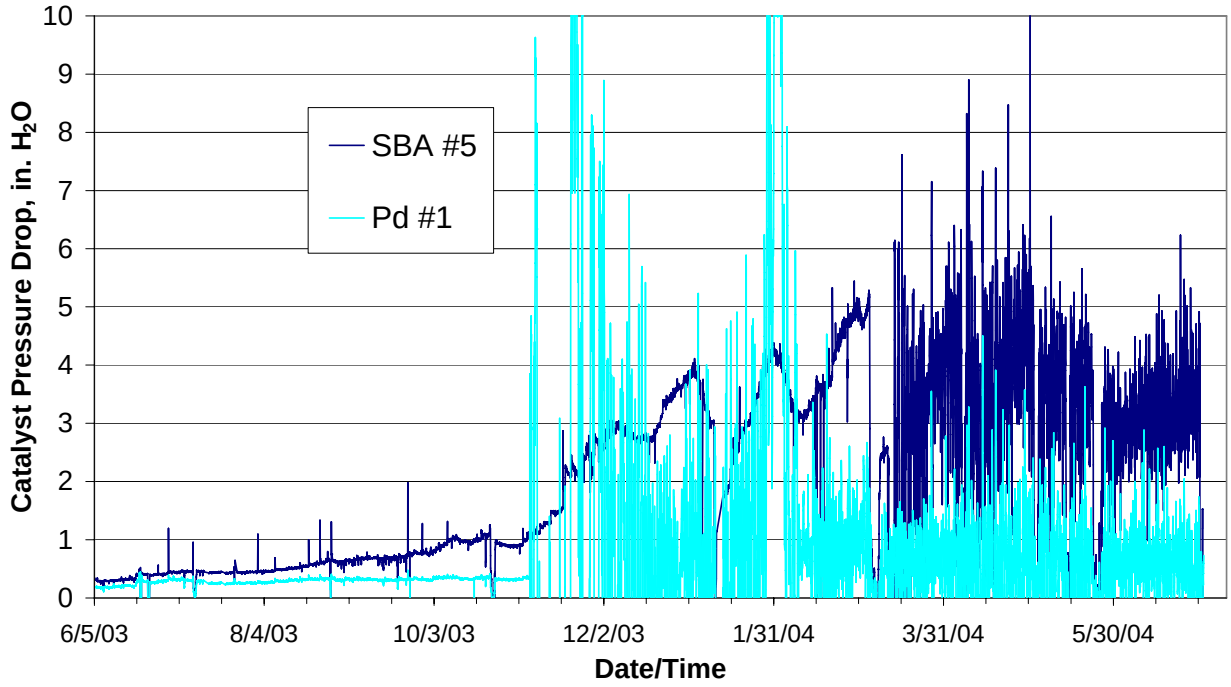

Figure 4-17
Pressure-drop Data for the Catalysts in Service at CCS through June 2004

The SBA #5 pressure drop averaged between 3 and 5 in. H_2O during the last six months of operation. This is more than ten times the initial pressure drop on June 5, 2003. It is possible that there is particle-to-particle electrostatic attraction between the fly ash in the flue gas treated and the fly ash imbedded in the catalysts. Because this catalyst type is produced from a single fly ash source and is available in limited quantities, it is of lesser interest for future commercial

applications. So, regardless of the cause, the pressure-drop increase across this catalyst chamber is not of great concern.

As seen in Figure 4-17, the average pressure drop across the Pd #1 remained below 1 in. H_2O, indicating the effectiveness of the sonic horn in preventing fly ash buildup across this catalyst. The other two catalysts appeared to have similar pressure-drop values to those of Pd #1.

Although the sonic horns appear to be effective, these results suggest that a coarser catalyst pitch and higher superficial velocities through the catalyst chamber might help avoid fly ash buildup. Because the empty chambers were somewhat oversized to allow flexibility in the amount of catalyst installed in each, the flue gas velocities through the empty portions are quite low. At 2000 acfm (3400 m^3/hr), the gas velocity is 3.1 ft/sec (0.95 m/s), and at 1500 acfm (2550 m^3/hr) the velocity is only 2.3 ft/sec (0.70 m/s). Also, the reduced pressure drop and fly ash buildup for the SCR catalyst, which was installed as a single catalyst block, compared to that for the Pd #1 and SBA #5 suggests that a single catalyst layer rather than three individual layers would be a preferred configuration.

CCS Catalyst Activity Results

As described above, starting June 5, 2003, the sonic horns installed on the pilot unit at CCS appeared to be keeping the catalysts free of fly ash buildup. A catalyst performance measurement trip was conducted the next week (June 11-12) after one week in operation with the horns. Follow-up catalyst activity measurements were made in July, October, and December of 2003, and in February and June of 2004. The results from these measurement trips (all using the EPRI Hg SCEM for measurements) are discussed in the following paragraphs.

Table 4-16 summarizes the results from the June 2003 catalyst activity measurement trip. Results are shown for two flue gas flow rates through each catalyst chamber. The results showed that the Pd #1 remained highly active (>90% elemental mercury oxidation at 2000 acfm) and that the new catalyst (C #6) was very active (>97% oxidation). Both of these catalysts were still adsorbing some Hg at the time of these measurements (~15% adsorption by the Pd, 25% by the C #6), so these results might have been biased slightly. The SCR catalyst and SBA #5 fly ash catalyst results were less encouraging. Those catalysts were measured at about 50% oxidation at their normal flue gas flow rates.

The next catalyst activity measurement trip was made during the week of July 21. The pilot unit was found off line the morning of July 21 due to a power loss to the unit over the weekend. The pilot unit was restarted, but it is possible that some mercury desorbed from the catalysts during this period with no flue gas flow, causing some adsorption of mercury after gas flow resumed to restore adsorption equilibrium.

Table 4-16
Summary of Catalyst Activity Results from CCS, June 2003 (Hg concentrations reported as measured, uncorrected for sample gas O_2 content)

Sample Location	Total Hg Concen-tration ($\mu g/Nm^3$)*	Hg^0 Concen-tration ($\mu g/Nm^3$)*	Overall Hg Oxidation (% of total)	Observed Hg Adsorption across Catalyst (%)	Hg^0 Oxidation across Catalyst (%)	Flue Gas Flow Rate (acfm) [m^3/hr]	Catalyst Area Velocity (sft/hr) [Nm/h]
Normal Flow Rate Results:							
Pilot Unit Inlet	10.2	7.29	29	NA**	NA	NA	NA
SBA #5 outlet	9.88	4.76	52	3.0	52	2000 [3400]	33 [9.4]
SCR outlet	10.0	5.26	48	1.7	47	1500 [2550]	14 [4.0]
C #6 outlet	7.74	0.22	97	24	98	2000 [3400]	30 [8.5]
Pd #1 outlet	8.60	0.75	91	16	92	2000 [3400]	49 [14]
Alternate Flow Rate Results:							
Pilot Unit Inlet	10.4	7.29	30	NA	NA	NA	NA
SBA #5 outlet	9.88	3.79	62	4.7	62	1500 [2550]	25 [7.1]
SCR outlet	10.0	5.44	46	3.4	45	960 [1600]	9.1 [2.6]
C #6 outlet	7.74	0.21	97	25	98	2500 [4250]	38 [11]
Pd #1 outlet	8.60	1.09	87	17	89	2500 [4250]	61 [17]

* Note: 1.0 $\mu g/Nm^3$ ~ 0.8 lb Hg per 10^{12} Btu heat input
**NA – Not applicable.

The results of the catalyst activity measurements (by SCEM) are shown in Table 4-17. As was expected, all four catalysts appeared to have been adsorbing a small amount of mercury from the inlet flue gas, ranging from 5% apparent adsorption by the SCR catalyst to 32% adsorption for the C #6 catalyst. The activity of the C #6 and Pd #1 catalysts remained high, at greater than 90% Hg^0 oxidation across the C #6 catalyst and greater than 80% Hg^0 oxidation across the Pd #1. However, the measured activity for each was lower than was measured in June. The activity of the SBA #5 and SCR catalysts continued to decline over time, to about 40% Hg^0 oxidation across the SBA #5 catalyst and 20% oxidation across the SCR catalyst.

Table 4-17
Oxidation Catalyst Activity Results for CCS Pilot, July 2003 (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Results from 7/22/03:					
Pilot Inlet	15.8	11.3	-	-	28
SBA #5 Outlet	13.5	6.92	15	39	49
C #6 Outlet	10.7	0.73	32	94	93
Results from 7/23/03:					
Pilot Inlet	14.9	11.1	-	-	25
SCR Outlet	14.3	8.74	5	21	39
Pd #1 Outlet	12.6	1.89	15	83	85
SBA #5 Outlet	-	6.59	-	39	-
C #6 Outlet	-	0.78	-	93	-

* Note: 1.0 μg/Nm^3 = 0.67 lb Hg per 10^{12} Btu heat input

Prior to the July 2003 measurement trip, sample gas oxygen concentrations were not routinely measured, other than spot checks to ensure there were no significant sample leaks. All mercury concentrations were reported on an as-measured basis, as is the case for Tables 4-12 through 4-16 in this report. Since there is no significant source of air inleakage across the oxidation catalyst pilot chambers, there was no need to correct measured inlet and outlet mercury concentrations to a common O_2 level to calculate catalyst performance. In mid-2003, the Hg SCEMs were modified to measure O_2 as well as mercury concentrations on a semi-continuous basis. From that point on, sample gas mercury concentrations were typically corrected to a common O_2 level, typically 3%, for reporting purposes. Correcting all results to a common O_2 basis offers several advantages over reporting as-measured values, such as allowing for a constant factor for converting mercury concentration data to an equivalent lb/trillion Btu heat input basis. The results in Table 4-17 and all flue gas mercury concentration data shown in this report that were collected after July 2003 are correspondingly reported as corrected to a 3% O_2 concentration.

Two catalyst activity measurement trips were made to CCS during the last quarter of calendar year 2003, one the week of October 6 and the second the week of December 15. The results of those catalyst activity measurements (by SCEM) are shown in Table 4-18.

Table 4-18
Oxidation Catalyst Activity Results for CCS Pilot, October and December 2003 (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Results from 10/8/03:					
Pilot Inlet	19.5	14.2	-	-	27
SBA #5 Outlet	17.4	8.11	11	43	53
SCR Outlet	17.8	10.2	9	28	43
C #6 Outlet	16.6	1.62	15	89	90
Pd #1 Outlet	16.4	3.72	16	74	77
Results from 10/9/03:					
Pilot Inlet	-	12.3	-	-	-
SBA #5 Outlet	-	6.46	-	47	-
SCR Outlet	-	7.99	-	30	-
C #6 Outlet	-	1.37	-	89	-
Pd #1 Outlet	-	3.26	-	73	-
Results from 12/16/03:					
Pilot Inlet	20.2	14.6	-	-	27
SBA #5 Outlet	19.3	10.2	4	30	47
SCR Outlet	19.6	9.66	3	34	51
C #6 Outlet	16.3	1.26	19	91	92
Pd #1 Outlet	18.2	3.59	10	76	80

* Note: 1.0 μg/Nm^3 = 0.67 lb Hg per 10^{12} Btu heat input

The inlet flue gas mercury concentrations were consistent between the two trips, with between 19 and 20 μg/Nm^3 of total mercury and 27% mercury oxidation. As was seen in the July results, all four catalysts still appeared to have been adsorbing a small amount of mercury from the inlet flue gas, ranging from 9% to 16% apparent adsorption in October and between 4 and 19% in December. The activity of the C #6 and Pd #1 catalysts remained relatively high, at about 90%

Hg^0 oxidation across the C #6 catalyst and 75% Hg^0 oxidation the Pd #1. However, the measured activity for each was slightly lower than was measured in July. The apparent activity of the SBA #5 and SCR catalysts continued to be lower than the C #6 and Pd #1 catalysts, in the range of 28% to 47% Hg^0 oxidation.

The next catalyst activity measurement trip was made to CCS on February 16, 2004. The results of the catalyst activity measurements (by SCEM) are shown in Table 4-19. The inlet flue gas mercury concentrations varied during the day, averaging about 14 μg/Nm^3 in the morning and 19 μg/Nm^3 of total mercury in the afternoon. At the higher inlet total mercury concentration, the observed pilot unit inlet mercury oxidation averaged 15%. As had been seen in previous results, all four catalysts appeared to be adsorbing a small amount of mercury from the inlet flue gas, ranging from 3% to 9% apparent adsorption. However, this small amount of mercury adsorption could be within measurement error given the fluctuating total inlet mercury concentrations seen over the course of the day.

Table 4-19
February 2004 Oxidation Catalyst Activity Results for CCS Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Results from 2/18/04 (a.m.):					
Pilot Inlet	14.7	16.0	-	-	**
SBA #5 Outlet	13.7	11.6	6.6	28	16
C #6 Outlet	13.8	2.07	6.5	87	85
Results from 2/18/04 (p.m.):					
Pilot Inlet	19.8	16.8	-	-	15
SCR Outlet	19.1	12.3	3.1	27	36
Pd #1 Outlet	17.9	5.70	9.4	66	68
Pilot Inlet	-	13.6	-	-	-
SBA #5 Outlet	-	10.5	-	23	-
C #6 Outlet	-	1.53	-	89	-

*Note: 1.0 μg/Nm^3 = 0.67 lb Hg per 10^{12} Btu heat input
**Value not calculated; observed mercury oxidation was less than 0% due to fluctuations in inlet total mercury concentrations during time period measurements were made.

The activity of the C #6 and Pd #1 catalysts remained relatively high, with 87 to 89% Hg^0 oxidation across the C #6 catalyst and 66% Hg^0 oxidation across the Pd #1. However, the measured activity for each was slightly lower than was measured last, in December 2003. The activities of the SBA #5 and SCR catalysts continued to be lower than the C #6 and Pd #1 catalysts, in the range of about 20% to 30% Hg^0 oxidation. The activity of both catalysts had dropped measurably since December.

The final catalyst activity measurement trip was made to CCS during the last week in June 2004. The results of the catalyst activity measurements (by SCEM) are shown in Table 4-20. The inlet flue gas mercury concentrations varied over the typical range for CCS, from about 15 $\mu g/Nm^3$ to over 17 $\mu g/Nm^3$ of total mercury. The observed pilot unit inlet mercury oxidation percentage ranged from 28 to 34%. As has been seen in previous results, three of the four catalysts appeared to be adsorbing a small amount of mercury from the inlet flue gas, ranging from 1% to 11% apparent adsorption. However, this small amount of mercury adsorption could be within measurement error given the fluctuating total inlet mercury concentrations seen over the course of a day.

The activities of the C #6 and Pd #1 catalysts remained relatively high, with 79% Hg^0 oxidation across the C #6 catalyst and 67% Hg^0 oxidation across the Pd #1 when measured at their normal flue gas flow rates of 2000 acfm each. The measured activity for the C #6 was several percentage points lower than was measured last, in February. Both catalysts showed a small increase in Hg^0 oxidation percentage when the flue gas flow rate was reduced to 1500 acfm.

The activities of the SBA #5 and SCR catalysts continued to be lower than the C #6 and Pd #1 catalysts, in the range of about 12% to 26% Hg^0 oxidation. The activity of the SBA #5 catalyst had dropped measurably since February, but the SCR catalyst was virtually unchanged.

The “clean catalyst” activity results for all four catalysts are plotted versus time in Figures 4-18 and 4-19. Some data points from late 2002 and early 2003, where the catalysts were obviously plugged with fly ash, have been edited from the plots. Activity results for the Pd #1 and C #6 catalysts are plotted in Figure 4-18 and results for SBA #5 and SCR catalysts in Figure 4-19. Within the range of measurement variability, the data plotted in Figure 4-18 show a linear downward trend in the catalyst activity versus time in service for the two more active catalysts. The June measurements were considered the “end of test” activity for the catalysts being tested at CCS, so the linear least squares fits of the data shown in the figure were used to make catalyst life projections.

The data plotted in Figure 4-19 show relatively “flat” activity performance for the SCR catalyst over time since the sonic horns were installed in June 2003, albeit at relatively low oxidation percentages. The apparent activity of the SBA #5 catalyst continually decreased with time since September 2003, most likely due to fly ash build up across this catalyst.

Table 4-20
June 2004 Oxidation Catalyst Activity Results for CCS Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Results from 6/26/04:					
Pilot Inlet	14.9	10.6	-	-	28
Pd #1 Outlet	14.4	3.51	3	67	76
Pd #1 Outlet (low flow, 1500 acfm)	13.2	3.39	11	68	74
Results from 6/27/04:					
Pilot Inlet	17.3	12.4	-	-	28
SCR Outlet	17.2	9.16	1	26	47
SCR Outlet (low flow, 1200 acfm)	16.8	10.7	4	13	36
Results from 6/28/04:					
Pilot Inlet	16.9	11.1	-	-	34
C #6 Outlet	16.4	2.35	3	79	86
C #6 Outlet (low flow, 1500 acfm)	15.8	1.88	4	83	88
Results from 6/28/04 (p.m.):					
Pilot Inlet	17.4	11.9	-	-	32
SBA #5 Outlet	16.9	10.4	0	12	40

* Note: 1.0 μg/Nm^3 = 0.67 lb Hg per 10^{12} Btu heat input

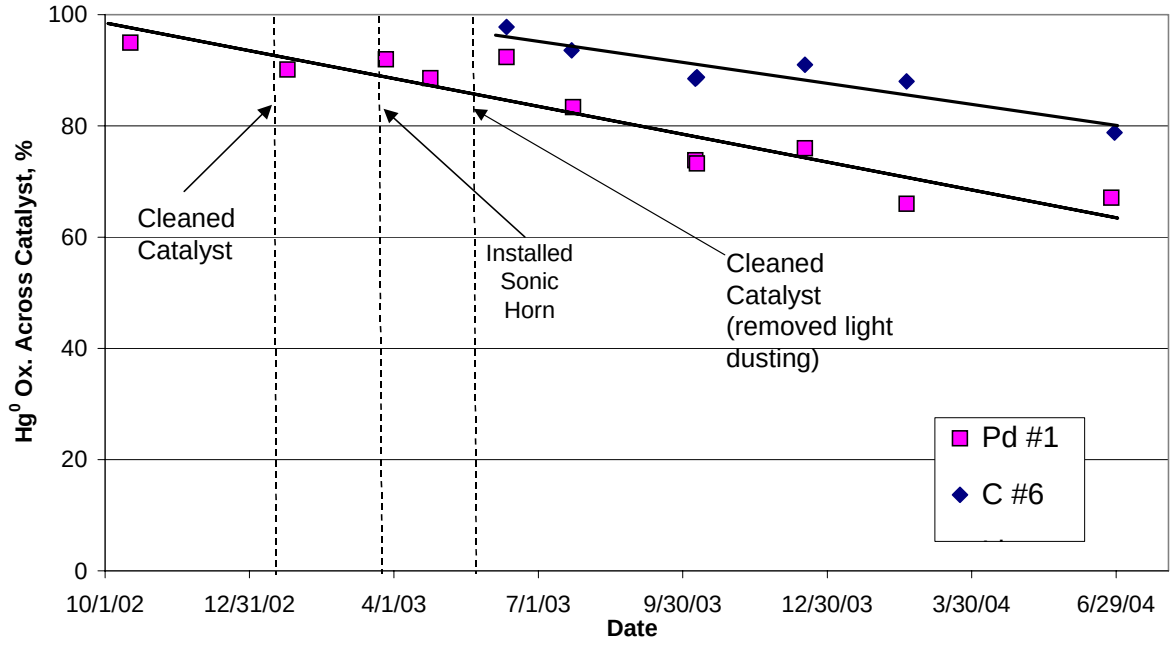

Figure 4-18
Activity for Hg^0 Oxidation versus Time for Pd #1 and C #6 Catalysts at CCS

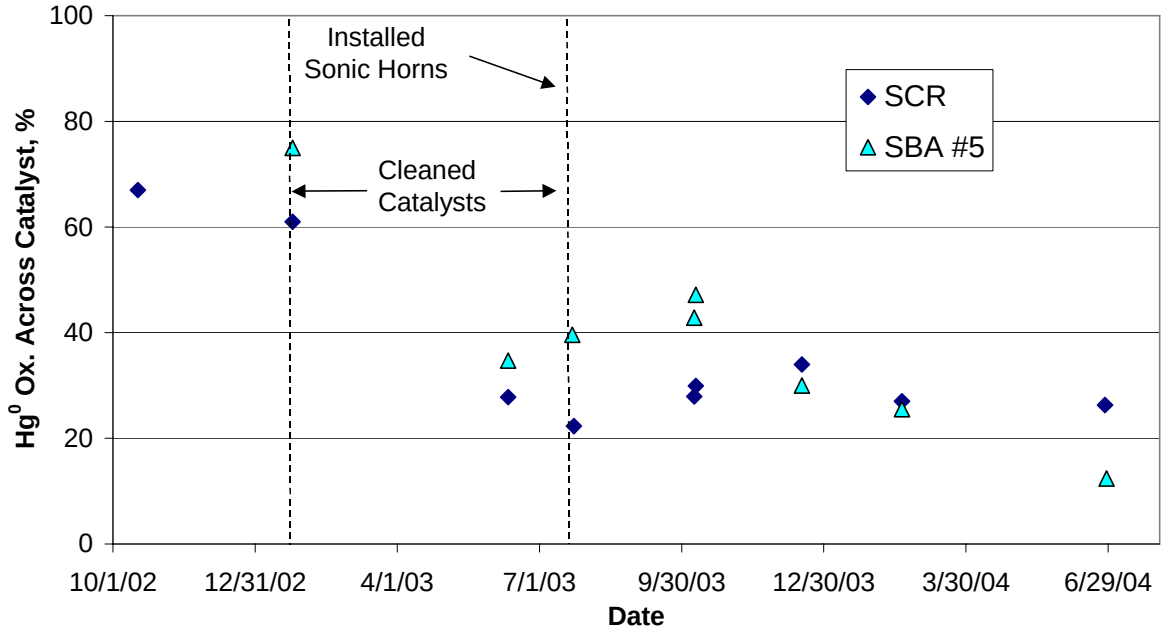

Figure 4-19
Activity for Hg^0 Oxidation versus Time for SCR and SBA #5 Catalysts at CCS

CCS Catalyst Regeneration Test Results

In July 2004, attempts were made to thermally regenerate the SCR and Pd #1 catalysts in situ. The attempted regeneration of the C #6 catalyst was delayed until September due to equipment and personnel scheduling issues. Each thermal regeneration was conducted by replacing the sonic horn on the inlet of that catalyst chamber with a 36-kW duct heater. The inlet flue gas flow to the compartment being regenerated was closed off, and an air supply was connected to the duct heater. This heated air was the only gas flow through the catalyst during regeneration. The duct heater outlet air temperature was controlled to 600^{o}F. This was set as the upper limit for the regeneration air temperature based on the temperature rating for the gasket material used to seal the compartment access covers. The regeneration air flow was limited by the heater capacity at about 280 acfm as measured downstream of the catalyst, at a maximum temperature of about 410 to 420^{o}F. This downstream temperature was also a constraint on the thermal regeneration, as the Teflon seats in the downstream catalyst chamber flow control valves could not exceed 450^{o}F. The difference between the inlet air temperature of 600^{o}F and the maximum outlet temperature achieved, 420^{o}F, was due to heat losses through catalyst chamber and outlet duct walls.

The hot air flow was allowed to continue through the afternoon the test started and overnight. Each regeneration period lasted 15 to 18 hours. After heating each catalyst with 600^{o}F air overnight, it was placed back in flue gas service. Catalyst activity was subsequently measured by SCEM to determine if the elemental mercury oxidation activity increased.

The results from these tests are summarized in Table 4-21. The results show that the activities of the Pd #1 and SCR catalysts improved measurably after the thermal regeneration. The Pd #1 activity improved to near the activity of the fresh catalyst (88% vs. 95%) while the SCR catalyst improved to about two-thirds of its original activity (46% vs. 67%). However, the C #6 catalyst showed no measurable improvement in activity after the thermal regeneration. It is possible that the species that cause activity loss by the C #6 catalyst are more strongly adsorbed to the carbon-based catalyst than to the metal-based catalysts.

Also shown in the table are data for total mercury breakthrough across the catalysts after regeneration, at the time their post-regeneration mercury oxidation performance was measured. For the Pd #1 and SCR catalysts, the mercury breakthrough was within the normal range for operating catalysts, indicating that the mercury oxidation performance measured was not likely biased significantly by mercury adsorption by the catalysts. For the C #6 catalyst, which is known to have a greater mercury adsorption capacity than the metal-based catalysts, the total mercury breakthrough was only 68%, indicating that measurable adsorption was still occurring across that catalyst. This suggests that the mercury oxidation activity of this catalyst could be biased high by adsorption of elemental mercury from the inlet flue gas. However, since this catalyst was not observed to improve in mercury oxidation activity upon regeneration anyway, such a bias would be of little consequence.

Some of the mercury oxidation activity results shown in Table 4-21 warrant further discussion. One is that the observed activity of the Pd #1 catalyst was measured to be higher prior to regeneration in late July than it had been at the end of the long-term pilot test in June. There is a

Table 4-21
Results of CCS Catalyst Regeneration Tests

Catalyst	Elemental Mercury Oxidation Across Catalyst, %				Total Mercury Breakthrough Across Catalyst (%)
	Fresh Catalyst (date)	End of Test (6/04)	Prior to Regeneration (date)	After Regeneration (date)	After Regeneration (date)
Pd #1	95 (10/02)	67	79 (7/04)	88 (7/04)	84 (7/04)
SCR	67 (10/02)	26	25 (7/04)	46 (7/04)	86 (7/04)
C #6	98 (6/03)	79	53* (9/04)	48(9/04)	68 (9/04)

*Estimated because there was not a catalyst inlet Hg^0 concentration measurement made near the time period the catalyst outlet was measured; catalyst inlet Hg^0 concentration was estimated from total Hg and assumed 34% oxidation.

probable explanation for this observation. The Pd #1 catalyst material had been observed to readily regenerate in the past, during NETL project DE-AC22-95PC95260, often improving in performance just by removing the catalyst from flue gas exposure. During the time elapsed between when the long-term test ended and the regeneration tests were conducted, the pilot unit was shut down several times, and ambient air was allowed to enter the catalyst chambers while new ports were welded onto the catalyst outlet duct to accommodate pilot wet FGD tests. It is likely that the species that reduce the activity of the Pd #1 desorbed to some extent just by stopping flue gas flow through the catalyst several times and exposing the catalyst to ambient air.

As noted in Table 4-21, an estimate was required for the oxidation across the C #6 catalyst prior to regeneration because there was not a catalyst inlet elemental mercury concentration measurement near the time the outlet was measured. A review of the data showed that the inlet total mercury concentration had changed since the time the catalyst inlet elemental mercury concentration was measured. Consequently, the catalyst inlet elemental mercury concentration at the time the outlet was measured was estimated from the inlet total measured near that time multiplied by an assumed inlet oxidation percentage of 34%. This value was interpolated between the oxidation measured before (36%) and after the regeneration was completed (32%).

Assuming this estimate for the C #6 catalyst is reasonably accurate, the activity prior to regeneration (53%) was lower than the end of test value from June (79%). During the three months that elapsed between the end of the long-term test and when this regeneration test was conducted, the pilot unit was shut down and restarted a number of times, and operated for several periods with flue gas flow through the catalysts but without the sonic horns in service. It is possible that the C #6 catalyst became partially plugged with fly ash over this period. In fact, when the catalysts were later recovered from the pilot unit, all three of the remaining catalysts were observed to have significant fly ash buildup that may have occurred during this final three months.

The most important note about these regeneration test results is that they were intended to be "proof of concept" tests to determine if the catalysts could be thermally regenerated. The conditions were not optimized to ensure the effectiveness of the thermal regeneration. For example, it is known that the air entering the catalyst chamber was at 600°F, and that the air in the 6-in. discharge piping from the catalyst chamber reached a maximum of 410 to 420°F, but it is not known what actual maximum temperature was achieved at the catalyst surfaces. Also, the regeneration air flow of approximately 280 acfm was much lower than the normal flue gas flow through these catalysts (1500 to 2000 acfm), and the regeneration air flow was introduced from the top surface of the catalyst chamber inlet transition duct rather than through the centered inlet duct run. Because of this, it is possible that only portions of the catalysts saw appreciable regeneration air flow. In future regeneration tests, it is recommended that a larger heater be used, to allow a greater air flow that will better distribute across the catalyst cross section, and that thermocouples be retrofitted to the catalyst chamber to allow temperatures to be monitored across the cross section of the catalyst outlet plane.

Furthermore, these regeneration tests were run in batch mode, with the heated air at 600°F flowing through the catalyst chambers overnight. Thus, these results do not indicate what is the minimum heating period required or the optimum air temperature to regenerate the catalysts.

CCS Flue Gas Characterization Results

Part of the long-term oxidation catalyst pilot test effort at CCS included characterizing the flue gas treated by the pilot unit. Over nearly 21 months of long-term catalyst testing, several flue gas characterization efforts were conducted. The measurements included:

- CCS FGD system inlet and outlet mercury concentrations by the Ontario Hydro method,
- Pilot unit inlet and catalyst outlet mercury concentrations by the Ontario Hydro method (three times),
- Pilot unit inlet metals by Method 29,
- Pilot unit inlet halogens by Method 26a,
- Pilot unit inlet and catalyst outlet sulfuric acid by the Controlled Condensation method, and
- Pilot unit inlet and catalyst outlet NO and total NO_X (once by the gas detection tube method and once by CEM).

These results are presented and discussed in the following paragraphs.

Ontario Hydro Results – October 2002

Table 4-22 summarizes the results of measurements made at CCS by the Ontario Hydro method in October 2002, at the full-scale FGD inlet and outlet locations, and at the catalyst inlet and the outlet of the two catalysts that were in service at that time. The results show that the mercury in the FGD inlet/pilot unit inlet flue gas at CCS is not very highly oxidized (less than 50% oxidation), and that the total mercury concentrations are typically in the range of 10 to 20 μg/Nm^3. This agrees with the measured coal mercury concentration of 0.08 mg/kg. Combustion calculations using this coal mercury concentration predict a flue gas concentration of 15 μg/Nm^3, assuming all of the coal mercury is present in the gas phase at the FGD inlet.

Table 4-22
Summary of Ontario Hydro Results from CCS, October 2002 (all values represent the average from three individual measurement runs; reported at actual duct concentrations, uncorrected for O_2)

	Hg Concentration (μg/Nm^3)*			Total Hg Oxidation (%)	Hg^0 Oxidation Across Catalyst (%)
	Hg^{+2}	Hg^0	Total		
FGD Inlet	7.1	11.6	18.7	38	-
FGD Outlet	0.2	11.7	11.8	1.4	-
Pilot Inlet	6.0	11.3	17.3	35	-
Pilot Outlet:					
SCR Catalyst (1500 acfm [2550 m^3/hr])	11.5	3.5	15.0	77	69
Pd #1 Catalyst (2000 acfm [3400 m^3/hr])	15.4	0.7	16.1	96	94

* Note: 1.0 μg/Nm^3 ~ 0.8 lb Hg per 10^{12} Btu heat input

The data show that oxidized mercury is removed across the FGD absorbers at high efficiency (almost 98% removal) and that little or no elemental mercury is re-emitted. That is, the increase in elemental mercury concentration across the FGD absorber is negligible (a measured 0.6% increase in concentration, or an increase of less than 0.1 μg/Nm^3, which is well within the precision of the measurement method). The overall mercury capture across the FGD absorbers was 37%.

Table 4-23 compares the Ontario Hydro method results for the pilot unit to those measured by the Hg SCEM during the same time period. These results show excellent agreement between the Hg SCEM and the Ontario Hydro method. The measured total mercury concentrations at each of the three pilot unit measurement locations were very close between the two methods, and the measured elemental mercury oxidation percentages across the two catalysts also agreed well.

Table 4-23
Comparison of Ontario Hydro Results with EPRI Mercury Semi-continuous Emissions Monitor Results from CCS, October 2002 (Hg concentrations reported at actual duct concentrations, uncorrected for O_2)

	Hg Concentration (μg/Nm^3)*			Total Hg Oxidation (%)	Hg^0 Oxidation Across Catalyst (%)
	Hg^{+2}	Hg^0	Total		
Pilot Inlet – OH	6.0	11.3	17.3	35	-
Pilot Inlet – SCEM	7.5	9.1	16.6	45	-
Pilot Outlet:					
SCR Catalyst – OH (1500 acfm [2550 m^3/hr])	11.5	3.5	15.0	77	69
SCR Catalyst – SCEM (1500 acfm [2550 m^3/hr])	12.7	2.9	15.6	81	68
Pd #1 Catalyst – OH (2000 acfm [3400 m^3/hr])	15.4	0.67	16.1	96	94
Pd #1 Catalyst – SCEM (2000 acfm [3400 m^3/hr])	15.2	0.85	16.1	95	91

* Note: 1.0 μg/Nm^3 ~ 0.8 lb Hg per 10^{12} Btu heat input

Some relative error is seen when comparing the pilot unit inlet oxidation percentages between the two methods. However, some error might be expected considering that the Ontario Hydro method takes an integrated, speciated sample at each location over the sampling period while the Hg SCEM had to cycle through three measurement locations and between elemental and total mercury measurements over that same period. The SCEM data may reflect temporal changes in inlet flue gas speciation that were averaged over time in the Ontario Hydro results. Because of this difference between how SCEM data and Ontario Hydro data are collected, there will always be a level of uncertainty between the two types of measurement results, depending on how variable the mercury concentrations and speciation are for the flue gas being sampled.

Ontario Hydro Results – July 2003

As discussed above, in the October 2002 relative accuracy tests, measured across the Pd #1 and SCR catalysts, the Hg SCEM and OH measurements were almost identical. However, in the July 2003 relative accuracy tests across all four catalysts, there were significant differences between the measurement results by the two methods. This comparison is made in Table 4-24. For clarity, the OH results at each location are shown in bold text, while the SCEM results at each location are shown in normal text.

At the pilot unit inlet, the SCEM results showed 15 to 27% lower concentrations for both total and elemental mercury than did the OH results, but the inlet flue gas mercury oxidation percentages were similar for both measurement types (approximately 25%). The oxidized mercury concentration measured by the two methods compared more favorably, with the SCEM results being within 1 to 2% of the OH concentrations. This relatively consistent bias seen in the comparison of results for the two methods at the pilot unit inlet is not a significant concern for this project, which is determining the change in mercury oxidation across catalysts. Obviously, a difference of 15 to 27% between two measurement methods could become an issue if these measurements were being used for compliance purposes.

Table 4-24
Comparison of Ontario Hydro Results with EPRI Mercury Semi-continuous Emissions Monitor Results from CCS, July 2003 (all values corrected to 3% O_2 in flue gas)

		Hg Concentration (μg/Nm^3)			Total Hg Oxidation (%)	Hg^0 Oxidation Across Catalyst (%)
		Hg^{+2}	Hg^0	Total		
Pilot Inlet – 7/22	**OH**	**4.57**	**13.8**	**18.4**	**25**	**-**
	SCEM	4.49	11.3	15.8	28	-
Pilot Inlet – 7/23	**OH**	**3.78**	**15.2**	**18.9**	**20**	**-**
	SCEM	3.83	11.1	14.9	25	-
Pilot Outlet:						
SBA #5 – 7/22 (2000 acfm) [3400 m^3/h]	**OH**	**12.5**	**4.28**	**16.8**	**75**	**69**
	SCEM	6.53	6.92	13.5	49	39
SCR – 7/23 (1500 acfm) [2550 m^3/h]	**OH**	**15.8**	**1.32**	**17.1**	**92**	**92**
	SCEM	5.51	8.75	14.3	39	21
C #6 – 7/22 (2000 acfm) [3400 m^3/h]	**OH**	**16.0**	**0.34**	**16.3**	**98**	**98**
	SCEM	10.0	0.73	10.7	93	94
Pd #1 – 7/23 (2000 acfm) [3400 m^3/h]	**OH**	**15.3**	**1.78**	**17.1**	**90**	**90**
	SCEM	10.7	1.89	12.6	85	83

* Note: 1.0 μg/Nm^3 = 0.67 lb Hg per 10^{12} Btu heat input

At the catalyst outlets, the total mercury concentrations were lower in the SCEM results than in the OH results, as was seen for the pilot unit inlet measurements. However, the elemental mercury concentration measurements for three of the four catalyst outlets were significantly higher in the SCEM results than in the OH results, which runs opposite the trend seen at the pilot inlet. For one catalyst (Pd #1) the elemental mercury concentrations measured by the two methods were similar.

With the catalyst outlet total mercury values being lower in the SCEM results than in the OH results while the elemental mercury concentrations were higher than the OH results, the SCEM results at the catalyst outlets showed significantly lower oxidized mercury concentrations and lower oxidation percentages than in the OH results. Similarly, the SCEM results showed lower elemental mercury oxidation percentages across the catalysts than in the OH results. In the case of the SCR catalyst, the difference between the two method results for elemental mercury oxidation across the catalyst was quite significant, with the OH method indicating 92% oxidation while the SCEM showed only 21%.

One's first inclination is to suspect the SCEM rather than OH method results as being erroneous, since the OH method is a specified ASTM method for mercury concentration measurements in flue gases from coal firing. However, for the SCR catalyst, it is the OH results that appear to be suspect. In October 2002, both the OH and SCEM results for that catalyst showed between 65 and 70% oxidation of elemental mercury across the catalyst. Since that time, the Hg SCEM showed a steady decrease in oxidation activity for this catalyst when in a "clean" condition (no fly ash buildup). The elemental mercury oxidation seen across this catalyst in the July 2003 OH results (92%) is significantly higher than in the initial OH results for this catalyst from October 2002. It is unlikely that the catalyst activity improved markedly after nine months of operation in flue gas. In fact, fly ash buildup and/or the adsorption of other species from the flue gas onto active catalytic sites would expectedly result in a loss of activity over this time period. Therefore, the OH results for the SCR catalyst outlet location appear to be suspect.

It is not apparent what might have caused the bias seen in the comparison of results from the two methods. Since the catalyst outlet elemental mercury numbers are lower in the OH results than in the SCEM results, one might suspect a sample train leak or some effect that caused poor capture of elemental mercury in the OH measurement train. However, the total mercury concentrations measured by the OH method at the catalyst outlets are quite consistent, and close to the totals measured at the inlet, so neither of these potential problems is evident. In the SCEM results, the total mercury concentrations are lower than in the OH results, which could indicate a sample train leak or adsorption of mercury somewhere in the sample train. However, neither of these potential problems could explain the higher elemental mercury concentrations measured by the SCEM compared to the OH results.

Under some sampling conditions, the inertial gas separator used in the pilot unit to separate any fly ash from the sample gas upstream of the gas conditioning impingers has been reported by other researchers to oxidize a portion of the elemental mercury in the sample gas. However, this effect runs opposite the observed bias, where the oxidation percentages measured at the catalyst outlets were typically lower in the SCEM results than in the OH results.

There are no known differences in SCEM operation between October 2002 and July 2003, but two known differences between the October and July OH measurement efforts. One is that in October, sodium thiosulfate was added to the KCl solution in the OH train based on advice attributed to Jeff Ryan of EPA.[9] The thiosulfate was reportedly added to quench free chlorine in the sample gas. For the July 2003 measurements, the OH method had been standardized as an ASTM method, so the ASTM method (which does not include thiosulfate addition to the KCl

solution) was employed.[5] The significance of this change is not thought to be significant, as there is very little free chlorine in the flue gas at CCS (see Method 26a results below).

The second difference, which is also not thought to be significant, is that in July the KCl solutions were mixed at 86% of the ASTM-specified concentration due to a math error in calculating the KCl reagent mass needed. This error, if it had been significant, would have reduced the oxidized mercury recovery in the OH train, which was not apparent in the results.

Ontario Hydro Results – June 2004

In June 2004, a third set of Ontario Hydro (OH) relative accuracy tests were conducted, across the Pd #1, SCR and C #6 catalysts, during simultaneous measurements with the mercury SCEM. These results are reported below in Table 4-25. Triplicate, simultaneous Ontario Hydro measurements were made across each catalyst module, using separate gas sampling trains located at the inlet and outlet of each of the respective catalyst boxes.

Table 4-25
June 2004 Ontario Hydro Relative Accuracy Results for CCS Pilot Compared to Hg SCEM Results

Parameter	Total Hg	Elemental Hg	Oxidized Hg
Pd #1 Catalyst, June 26, 2004			
Catalyst Inlet – OH, μg/Nm^3*	14.7	10.3	4.33
Catalyst Inlet - SCEM, μg/Nm^3	13.2	9.53	3.68
Relative Accuracy, %	-10.0%	-7.9%	-15.0%
Catalyst Outlet - OH, μg/Nm^3	14.59	3.32	11.27
Catalyst Outlet - SCEM, μg/Nm^3	12.78	3.11	9.67
Relative Accuracy, %	-12.4%	-6.2%	-14.2%
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	68	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	67	-

Table 4-25 (continued)
June 2004 Ontario Hydro Relative Accuracy Results for CCS Pilot Compared to Hg SCEM Results

Parameter	Total Hg	Elemental Hg	Oxidized Hg
SCR Catalyst, June 27, 2004			
Catalyst Inlet - OH, μg/Nm^3	15.2	11.3	3.86
Catalyst Inlet - SCEM, μg/Nm^3	15.4	11.0	4.38
Relative Accuracy, %	1.4%	-2.7%	13.5%
Catalyst Outlet - OH, μg/Nm^3	14.1	3.41	10.6
Catalyst Outlet - SCEM, μg/Nm^3	15.3	8.14	7.15
Relative Accuracy, %	8.8%	138.9%	-32.8%
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	70	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	26	-
C #6 Catalyst, June 28, 2004			
Catalyst Inlet - OH, μg/Nm^3	15.8	12.1	3.68
Catalyst Inlet - SCEM, μg/Nm^3	15.0	9.89	5.12
Relative Accuracy, %	-5.2%	-18.5%	39.0%
Catalyst Outlet - OH, μg/Nm^3	14.3	0.75	13.6
Catalyst Outlet - SCEM, μg/Nm^3	14.6	2.09	12.5
Relative Accuracy, %	2.1%	178.5%	-7.7%
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	94	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	79	-

*Note – All concentrations corrected to 3% O_2, dry basis; 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

The results for the Pd #1 catalyst show reasonably good agreement, with the SCEM results showing a small, but consistent negative bias compared to the Ontario Hydro results (-6 to -12% for the total and elemental Hg measurements). This error could have been introduced by a single error such as a 5 to 10% calibration error in the mass flow meter used in the SCEM, or by the cumulative effects of several small errors.

For the other two catalysts, the total mercury concentration measurements agreed very well, with relative accuracy percentages ranging from –5.2% to +8.8%, as did the catalyst inlet speciation.

The catalyst outlet mercury speciation results did not agree as well. As was seen in the second set of OH relative accuracy tests at CCS in July 2003, the OH results show much lower catalyst outlet elemental Hg concentrations than the SCEM results for these two catalysts. In both the July 2003 and June 2004 data, the outlet elemental Hg concentrations from the Pd #1 catalyst agreed reasonably well between the two methods.

As was discussed above, the authors believe the SCEM results are a better indicator of catalyst performance for the SCR and C #6 catalysts, but have no clear explanation why this bias exists. The most convincing evidence that the bias exists with the OH method rather than the SCEM data is seen in comparing the OH results from the three sets of OH measurements at CCS. The first set, in October 2002, showed 69% oxidation of elemental mercury across the SCR catalyst, which had only been in service for only two weeks. The second measurement, in July 2003, showed 92% oxidation across the catalyst, which is an unlikely increase after nine months in flue gas service. The third measurement, in June 2004, showed 70% oxidation across the SCR catalyst, still slightly higher than what was measured for the fresh catalyst.

Flue Gas Metals (Method 29)

Table 4-26 summarizes the results of flue gas metals concentration measurements made at CCS in October 2002 by Method 29. The results in the table represent averages of three individual measurement runs. Also shown in the table are gas phase metals concentrations measured at three sites at which mercury oxidation catalysts were previously evaluated in a DOE project (DE-AC22-95PC95260), but at a smaller scale.[2] Site 1 fires a Texas lignite fuel, Site 2 fires a PRB coal, and Site 3 fires an eastern bituminous coal.

Table 4-26
Flue Gas Metals Concentrations at CCS by Method 29 (Pilot Unit Inlet Location) – all values in ppbv (dry gas basis)

Metal	Site 1 Gas Phase Concentration	Site 2 Gas Phase Concentration	Site 3 Gas Phase Concentration	CCS Gas Phase Concentration	CCS Particulate Phase Concentration*
Aluminum	20.2	10.2	78.3	569	35.3
Antimony	0.17	0.07	0.14	0.71	0.49
Arsenic	ND	0.01	0.76	0.53	0.16
Barium	0.09	0.08	0.13	28.2	0.26
Beryllium	0.27	0.06	0.01	0.28	<0.77
Cadmium	0.05	0.02	0.01	<0.06	0.01
Calcium	41.0	15.7	18.9	509	121
Chromium	0.19	0.12	0.30	0.43	0.16

Table 4-26 (continued)
Flue Gas Metals Concentrations at CCS by Method 29 (Pilot Unit Inlet Location) – all values in ppbv (dry gas basis)

Metal	Site 1 Gas Phase Concentration	Site 2 Gas Phase Concentration	Site 3 Gas Phase Concentration	CCS Gas Phase Concentration	CCS Particulate Phase Concentration*
Cobalt	ND	0.02	0.05	<1.14	<1.18
Copper	0.48	0.56	0.12	0.39	1.32
Iron	9.08	8.62	18.8	146	19.3
Lead	0.11	0.05	0.05	0.12	0.04
Magnesium	3.02	3.05	3.64	177	11.3
Manganese	0.49	2.24	1.70	1.94	0.72
Molybdenum	0.01	0.02	0.08	1.13	<0.59
Nickel	0.41	0.17	0.85	1.48	0.15
Potassium	89.3	3.17	9.50	66.3	169
Selenium	26.8	2.94	45.3	0.70	0.51
Silver	0.01	0.01	0.03	<0.25	<0.05
Sodium	191	120	90.7	235	337
Strontium	0.09	0.04	0.20	-	-
Thallium	4.52	0.40	7.95	0.13	<0.14
Tin	-	-	-	0.34	18.8
Titanium	0.64	0.16	1.84	12.5	0.54
Vanadium	0.06	0.00	0.10	1.41	<1.37
Zinc	2.09	2.30	1.12	0.84	3.79

*Mass present in the particulate (solid phase) has been converted to an equivalent gas-phase concentration.

The results in Table 4-26 show that the flue gas at CCS contains considerably higher vapor-phase metal concentrations than the three previous sites for the following metals: aluminum, barium, calcium, iron, magnesium, molybdenum, nickel, titanium, and vanadium. Selenium, which was theorized to have played a role in the rapid loss of catalyst activity at Site 1 in the previous project,[2] was measured to be present at much lower concentrations at CCS than at any of the previous project sites.

Flue Gas Halogen Species (Method 26a)

Table 4-27 summarizes the results of flue gas halogen species concentration measurements made at CCS in October by Method 26a, along with results from the previous cooperative agreement. The results in the table represent averages of three individual measurement runs. As expected, the halogen species concentrations are quite low. In the CCS results, it is a bit surprising to see that the HF concentrations in the flue gas are higher than the HCl concentrations. In bituminous coals, the opposite is typically the case.

Table 4-27
Flue Gas Halogen Species Concentrations at CCS by Method 26a (Pilot Unit Inlet Location)

	Concentration (ppmv, dry basis unless noted otherwise)			
Species	**Site 1**	**Site 2**	**Site 3**	**CCS**
HCl	1.8	1.1 (wet basis)	79.1	1.56
Cl_2	NM*	1.2 (wet basis)	0.69	<0.04
HF	NM	NM	10.6	5.31
F_2	NM	NM	NM	0.12

*NM – Not measured

Compared to the flue gases at three previous sites where oxidation catalyst tests were conducted at smaller scale (Cooperative Agreement DE-AC22-95PC95260), the HCl concentrations at CCS are similar to those at Site 1 (Texas lignite) and Site 2 (PRB), but over an order of magnitude lower than at Site 3 (bituminous coal).[2] The chlorine (Cl_2) concentrations are lower than the values measured at the two previous sites where measured. The HF concentrations at CCS are lower than at Site 3, but were not measured at Sites 1 and 2 during the small-scale testing. Fluorine concentrations were not measured at any of the three previous sites.

Flue Gas Sulfuric Acid Concentrations (Controlled Condensation Method)

Flue gas sulfuric acid concentrations were measured for two reasons. One is that in the previous PRDA project, sulfuric acid was identified as a possible contributor to loss of mercury oxidation catalyst activity, perhaps due to adsorption or precipitation of sulfates that block active catalyst sites. Consequently, pilot unit inlet sulfuric acid concentrations were measured for comparison to values at other sites where mercury oxidation catalysts have been tested.

The second reason is that there has been some concern that catalysts active for oxidizing elemental mercury might also be active for oxidizing flue gas SO_2 to SO_3. SO_3 combines with flue gas moisture to form vapor-phase and/or condensed sulfuric acid. Sulfuric acid in the flue gas can lead to undesirable effects such as duct corrosion and increased plume opacity. Also, conversion of SO_2 to SO_3 could produce acid sulfates that can plug the honeycomb catalysts. Thus, oxidation of SO_2 to SO_3 across these mercury oxidation catalysts would be undesirable.

The results of the first set of flue gas sulfuric acid concentration measurements, by the Controlled Condensation method, are summarized in Table 4-28. Each data point represents the average of three runs. The average SO_2 concentration measured simultaneously over the course of the three Controlled Condensation runs at each location is also shown. The measured values agree reasonably well with the results of combustion calculations for a coal sample from October 21, 2002, which predict an SO_2 concentration of 940 ppmv (dry basis).

Table 4-28
Flue Gas Sulfuric Acid Concentrations at CCS by the Controlled Condensation Method

Location	Sulfuric Acid Concentration (ppmv, dry basis)	SO_2 Concentration (ppmv, dry basis)
Pilot Unit Inlet	0.21	933
SCR Catalyst Outlet	0.09	1040
Pd #1 Catalyst Outlet	0.04	836

The results in Table 4-28 do not indicate a percentage oxidation of SO_2 to SO_3 across these two catalysts, because the catalyst outlet sulfuric acid concentrations are slightly lower than the inlet values. This could indicate some adsorption of sulfuric acid across the catalysts, either on the catalyst substrate itself or on fly ash collected on catalyst surfaces, but could just as well represent run-to-run measurement variability. Based on prior experience, concentrations of 0.2 ppmv and lower represent a practical lower detection limit for the method, so the observed differences between the catalyst inlet and outlet concentrations may not be real.

In July 2003, the oxidation of SO_2 to SO_3/vapor phase sulfuric acid across the SBA #5 and C #6 catalysts was measured by conducting simultaneous Controlled Condensation measurements at the pilot unit inlet and outlet of each catalyst, in triplicate runs. The results of these measurements are summarized in Table 4-29, and, as for the SCR and Pd #1 catalysts above, show no significant oxidation across either catalyst (less than 0.1% conversion of SO_2 to SO_3). Also shown in the table are the flue gas SO_2 concentrations that were measured simultaneously at each measurement location.

Table 4-29
Summary of Measurements of SO_2 to SO_3 Oxidation Across the SBA #5 and C #6 Catalysts at CCS, July 2003

Location	Sulfuric Acid Concentration (ppmv, dry basis)	SO_2 Concentration (ppmv, dry basis)	Apparent SO_2 to SO_3 Conversion Across Catalyst (%)
Pilot Unit Inlet	0.35	1027	-
SBA #5 Catalyst Outlet	1.21	909	0.1
C #6 Catalyst Outlet	1.17	975	0.1

Flue Gas NO_2 Concentration

In October 2002, flue gas NO_2 concentrations were measured upstream of the pilot unit and downstream of the two installed catalysts using gas detection tubes. Similar to the potential for oxidation of SO_2 to SO_3 as discussed above, there was concern that the oxidation catalysts used in the pilot unit might catalyze the oxidation of NO to NO_2. While NO is a colorless gas, NO_2 has a brown color that can lead to flue gas plume coloration and increased opacity at concentrations as low as 10 ppm. Since significant oxidation of NO to NO_2 would be an undesirable side effect of mercury oxidation catalysts, this was an important measurement regarding the viability of a mercury oxidation process.

The project plan called for measurement of flue gas NO and NO_2 concentrations upstream and downstream of each catalyst using a continuous or semi-continuous NO_X analyzer. Since there would be a significant effort involved to temporarily set up this analyzer, and since only two of the four catalysts were in service in October 2002, it was decided to delay the analyzer measurements. Instead, gas detection tubes were used to provide an indication of any NO to NO_2 conversion across the two catalysts in service. Unfortunately, there is an interferent in the flue gas with the NO_2 detection tube, so changes in NO_2 concentration across the catalysts had to be determined by difference using NO and NO_X detection tubes. The results of these measurements are summarized in Table 4-30.

Table 4-30
Flue Gas NO_X Concentration Data Using Gas Detection Tubes

	NO_X (ppmv wet)	**NO (ppmv wet)**	**NO_2 (ppmv wet, by difference)**
Pilot Unit Inlet	150	150	0
SCR Catalyst Outlet	150	140	10
Pd #1 Catalyst Outlet	150	140	10

These results indicate the possibility that approximately 10 ppmv of the flue gas NO was oxidized to NO_2 across each catalysts (about 7% of the inlet NO). A concentration of 10 ppmv of NO_2 in the stack flue gas might result in some visible plume coloration. However, it is likely that some of the NO_2, if formed, would be scrubbed along with oxidized mercury in the downstream wet scrubber.

The apparent NO_2 concentrations shown in Table 4-30 were measured by a relatively imprecise method (the gas detection tubes results are read to the nearest 10 ppmv). Also, the NO_2 concentrations are calculated as the difference between two much larger numbers. Consequently, the indicated NO_2 concentrations should be considered to have a significant error band. It is estimated that the actual NO_2 concentrations downstream of the two catalysts were actually in the range of 0 to 20 ppmv.

After all four catalysts were in service, a NO_X analyzer was brought to the pilot unit site and set up to quantify NO and NO_2 concentrations upstream and downstream of all four catalysts on a

semi-continuous basis. The oxidation of NO to NO_2 across the catalysts was measured with a chemiluminescence NO_X gas analyzer that was cycled between the pilot unit inlet and the outlet gas from each of the four catalysts. The analyzer measured both NO and total NO_X at each location. These results are summarized in Table 4-31. No conversion of NO to NO_2 was measured across any of the four catalysts, as the NO and total NO_X concentrations were identical at each of the four outlet gas locations (the presence of NO_2 would be indicated by a measurable difference between these two values).

Table 4-31
Summary of Measurements of NO to NO_2 Oxidation Across the Hg^0 Oxidation Catalysts and SO_2 Concentrations at CCS, July 2003 (all measurements by portable CEM)

Location	NO (ppmv at 3% O_2)	NO_X (ppmv at 3% O_2)	Apparent Conversion of NO to NO_2 (%)	SO_2 (ppmv at 3% O_2)
Pilot Unit Inlet	137	137	0.00	1095
SBA #5 Outlet	134	134	0.00	1083
SCR Outlet	135	135	0.00	1065
C #6 Outlet	145	145	0.00	1083
Pd #1 Outlet	146	146	0.00	1097

The previous gas detection tube results from October 2002 indicated that possibly 0 to 20 ppmv of the flue gas NO was oxidized to NO_2 across the Pd #1 and SCR catalysts (about 7% of the inlet NO). A concentration of 10 to 20 ppmv of NO_2 in the stack flue gas might result in some visible plume coloration. However, the CEM data in Table 4-31 are believed to provide a better measure than gas detection tubes of whether NO_2 is formed, and these data show no NO_2 formation.

Spruce Pilot Test Program Results

The second pilot unit, which was built with EPRI funding to accelerate progress on the project, was completed in the first quarter of 2003 and shipped to the Spruce Plant in San Antonio, Texas in April. Plant personnel began installing the pilot unit adjacent to the west ID fan in June, and continued to work on the installation over the summer. The pilot unit installation was completed the week of August 11, and the pilot unit was started up on flue gas (without catalysts) that week. The first two catalysts, Pd #1 and Au, arrived from Süd-Chemie Prototech the week of August 18, and were installed the following week. The pilot unit was re-started with these two catalysts in place on August 28, and left in operation until the host unit came off line for a fall outage the evening of September 26. The outage continued until October 27, 2003.

The objectives of this initial one-month of operation were to ensure proper pilot unit operation, collect host site flue gas mercury concentration and speciation data, determine initial catalyst

activity for these two catalysts in the PRB flue gas, and to provide an indication whether sonic horns would be needed to avoid fly ash buildup on the catalysts at this site.

The pilot unit controlled temperature and flow rate through the catalyst chambers over this period, but a few problems were noted. One was that in the Texas climate and with the western exposure of the pilot unit, the temperature inside the pilot unit control box was going up well over 100°F, which is too hot for the electronic controls and data logging computer. To address this problem, a vortex cooler was retrofitted to the box. A second problem was that telephone communications with the pilot unit data logger could not be established due to line quality problems. The plant replaced the original line with shielded cable, and changed the source of the phone line connection in the plant to provide adequate signal quality. Other problems included a failed gauge-pressure transducer on one of the catalyst chambers, which was subsequently replaced, and a lack of differential indication from the catalyst chamber pressure-drop transducers. The latter was resolved by blowing out the pressure differential process tubing and ensuring that all of the valves on the pressure differential transducer valve blocks were in the correct position (open vs. closed, as appropriate).

Host site flue gas mercury concentration data were collected on three occasions over this initial period of operation, mid-August, early September, and late September 2003. These results are summarized in Table 4-32. The measurements at the pilot unit inlet showed much higher mercury oxidation percentages than were expected, typically over 75% oxidized rather than the expected 30% or less oxidized mercury as is typical of PRB flue gases. This was theorized to be an influence of the baghouse conditions at Spruce, which operates at a very low air-to-cloth ratio (less than 1.5 acfm/ft^2) [27 m/h], had aged bags (11 years old) and had a permanent dust cake that has possibly been influenced by pet coke co-firing (last fired December 2002). All of these effects could lead to increased mercury oxidation across the bags, such as due to increased gas/dust cake contact at the low air to cloth ratio and/or the influence of vanadium and/or unburned carbon in the permanent dust cake due to prior pet coke co-firing.

This theory was supported by measurements made at the baghouse inlet the week of September 22, using the EPRI Hg SCEM. These results are also included in Table 4-32. The baghouse inlet flue gas was found to have a total mercury concentration of 23 μg/Nm^3, with only 5% mercury oxidation. On the following day, the pilot unit inlet flue gas (downstream of the baghouse and ID fan) was found to have a total mercury concentration of 9 to 13 μg/Nm^3, with an average of 84 to 89% oxidation. This indicates both mercury removal and oxidation across the baghouse.

After these observations, data collected during the EPA Mercury Information Collection Request (ICR) were reviewed for mercury removal and oxidation across all of the baghouses that were sampled on pulverized coal fired units that fire low-sulfur Western subbituminous and bituminous coals (not including spray dryer/baghouse configurations).[1] Although the baghouse type was not identified with the ICR data, it is believed that all of these units have low air-to-cloth ratio, reverse gas baghouses such as at Spruce. These results are summarized in Table 4-33 and show that the values measured at Spruce are not unusual.

Table 4-32
Flue Gas Mercury Concentrations and Speciation at Spruce Plant (measured by Hg SCEM)

Date	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Hg Oxidation (%)
Pilot Unit Inlet:			
8/21/03	8.6	1.2	86
9/2/03	13.1	3.3	75
9/24/03 (a.m.)	9.5	1.6	84
9/24/03 (p.m.)	13.4	1.6	89
Baghouse Inlet:			
9/23/03	22.9	21.7	5

*Note – 1 μg/Nm^3 = 0.67 lb Hg/10^{12} BTU heat input

Table 4-33
Summary of ICR Results for Plants Firing Western Coals that have Fabric Filters for Particulate Control

Plant	Configuration	Hg Removal Across Fabric Filter (%)	Hg Oxidation at Fabric Filter Outlet (%)
Comanche 2	Pulverized-Coal Boiler, Fabric Filter	66 (based on FF inlet Hg)	87
Boswell 2	Pulverized Coal Boiler, Fabric Filter	83 (based on FF inlet Hg)	80
Intermountain	Pulverized Coal Boiler, Fabric Filter, Wet FGD	34 (based on coal Hg)	83
Valmont	Pulverized Coal Boiler, Fabric Filter	86 (based on FF inlet Hg)	82

Source: Reference 1

The pilot unit operated with two catalysts installed through September 26. Because of the pressure-drop transducer problem mentioned above, catalyst pressure-drop data were not available for this period. On September 25, after four weeks of operation, the pressure drop across each catalyst chamber was manually measured with a water manometer at about 0.25 in. H_2O [0.06 kPa], which is typical of these catalysts at this flow rate and in "clean" condition.

The pilot unit was brought off line on September 26 as the host unit came down for its fall outage, and inspected for fly ash buildup on September 29. Both chambers were very clean, with only a light dusting of fly ash. Figure 4-20 shows a close-up of one of the catalyst modules,

showing that it has very little fly ash buildup, and Figure 4-21 shows a view of the chamber floor, again showing very little fly ash buildup.

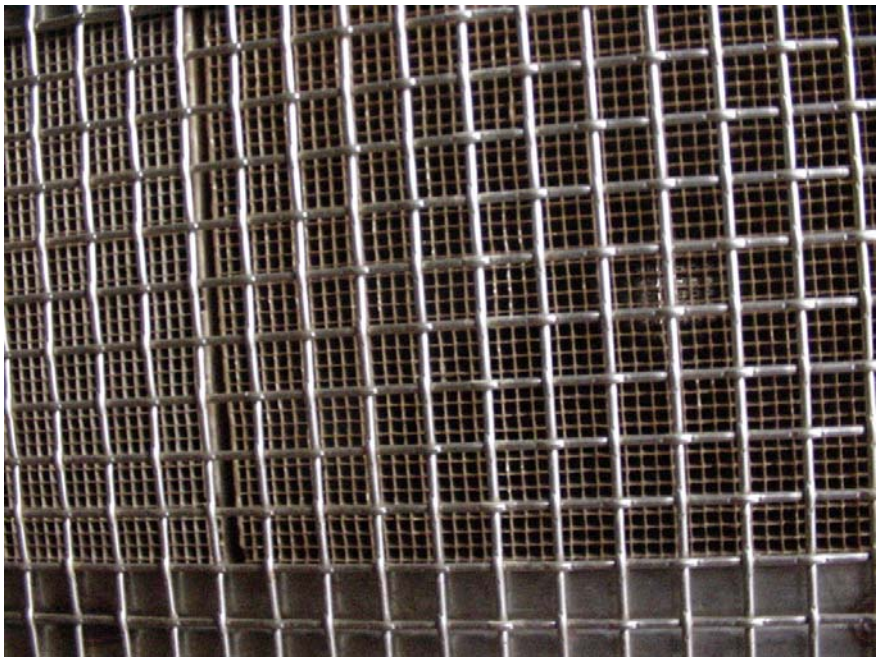

Figure 4-20
Close-up of One Catalyst Module after One Month of Operation at Spruce Plant

Figure 4-21
Photograph of a Catalyst Chamber at Spruce Showing Minimal Fly Ash Buildup after One Month of Operation

It was apparent that sonic horns would not be required at this host site, likely because it is downstream of a baghouse rather than an ESP as at Coal Creek. The baghouse presumably results in a lower dust loading in the pilot unit inlet flue gas, and a dust loading that has less residual electrostatic charge than in flue gas downstream of an ESP.

The host unit at Spruce Plant came back on line from its fall outage on October 27. The plan was to install the two remaining catalysts (SCR and C #6) in the pilot unit and restart operation soon after the host unit came on line. The installation of the two catalysts and the restart was delayed until the week of November 10 to allow time for the host unit to come back into stable operation and for plant craft personnel to work through remaining outage/startup issues. The pilot unit was restarted with all four catalysts installed on November 13. The few remaining problems with the catalyst pilot unit were corrected at this time.

Spruce Catalyst Pressure-drop Results

Figure 4-22 shows the pressure drop across the four catalyst chambers from November 13 through the end of calendar year 2003. The pressure-drop values were erratic through the end of November due to flow rate controller tuning problems. After the controllers were retuned to provide more steady flue gas flow rates, the pressure drop across each of the four catalyst modules also became steady. The pressure-drop values are all in the range of 0.2 to 0.3 in. H_2O [0.05 to 0.07 kPa]. Additional pressure-drop data have not been plotted, because the pressure-drop values for all four catalysts remained well below 1 in. H_2O (0.25 kPa) over nearly 18 months of catalyst operation.

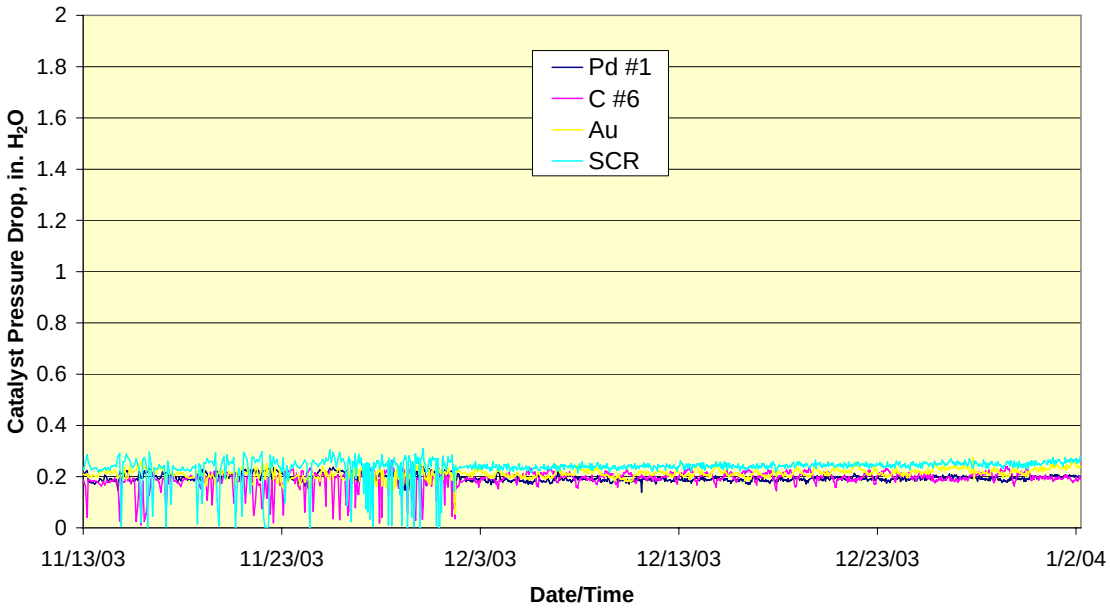

Figure 4-22
Pressure-Drop Data for the Catalysts in Service at Spruce through December
Note: 1 in. H_2O = 0.25 kPa.

Spruce Catalyst Activity Results

The first catalyst activity measurements were on September 2 and September 24, 2003, during the first month of operation with only two catalysts. These results are shown in Table 4-34. On September 2, after just a few days of catalyst operation, the pilot unit inlet total mercury was measured at 13 μg/Nm^3, while the total mercury at the two catalyst outlets were lower, at 7 to 11 μg/Nm^3, indicating that both catalysts were still adsorbing mercury from the flue gas. The inlet elemental mercury measured just over 3 μg/Nm^3, while the outlet of both catalysts measured about 0.5 μg/Nm^3. Ignoring possible effects from mercury adsorption, both catalysts appeared to be achieving greater than 80% oxidation of the inlet elemental mercury.

Table 4-34
September 2003 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst (%)	Apparent Hg^0 Oxidation Across Catalyst (%)	Overall Hg Oxidation Percentage
Results from 9/2/03 (2000 acfm through each catalyst):					
Pilot Inlet	13.1	3.3	-	-	75
Pd #1 Outlet	7.1	0.56	46	83	92
Au Outlet	11.1	0.53	14	84	95
Results from 9/24/03 (2000 acfm through each catalyst):					
Pilot Inlet	9.5	1.6	-	-	84
Pd #1 Outlet	9.7	0.28	-	82	97
Au Outlet	10.0	0.26	-	84	97
Results from 9/24/03 (1500 acfm through each catalyst):					
Pilot Inlet	13.4	1.6	-	-	89
Pd #1 Outlet	12.7	0.21	-	86	98
Au Outlet	13.5	0.26	-	83	98

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

On September 24, catalyst activity was measured at two flue gas flow rates, 2000 acfm [3400 m^3/h] through each catalyst in the morning and 1500 acfm [2550m^3/h] in the afternoon. In the morning, the inlet total mercury averaged about 10 μg/Nm^3, while the elemental mercury concentrations were measured at an average of 1.6 μg/Nm^3. The outlet elemental mercury

concentrations from both catalysts were approximately 0.3 μg/Nm^3, indicating 82 to 84% oxidation of elemental mercury across the catalysts. This is a low elemental mercury concentration compared to the sensitivity of the early-generation Hg SCEM being used at that time, so the accuracy of these outlet concentrations and the observed mercury oxidation percentages is in question. Neither catalyst appeared to be adsorbing any mercury.

In the afternoon, the pilot unit inlet total mercury concentrations increased to about 13 μg/Nm^3, although the average inlet elemental mercury concentration did not increase. At the lower flue gas flow rate of 1500 acfm [2550 m^3/h], the outlet elemental mercury concentrations from both the Pd #1 and gold catalysts were approximately 0.2 to 0.3 μg/Nm^3, indicating 83 to 86% oxidation of elemental mercury across each catalyst. Within the precision of these measurements, the performance of the two catalysts was identical, and neither catalyst showed a significant effect of the flow rate change.

Pilot unit inlet and catalyst outlet flue gas mercury concentration data were next collected December 10 through 12, approximately four weeks after the pilot unit was put back in service following the Spruce outage. By this time, all four catalysts were in service. The results are shown in Table 4-35. As did the results from September presented above, the measurements at the pilot unit inlet showed high mercury oxidation percentages, with 65 to 89% oxidized.

The results in Table 4-35 show quite a bit of scatter. On December 10, both the C #6 and gold catalysts appeared to be adsorbing mercury, but the next day they did not. The elemental mercury oxidation performance of these two catalysts also changed markedly from day to day, with the elemental mercury oxidation percentages across both catalysts being lower on December 11 than on December 10. On December 12, the Pd #1 and SCR catalysts showed similarly low oxidation performance, in the range of 50 to 55% oxidation of elemental mercury across the catalysts.

The reason for the poor measured performance for all four catalysts on December 11 and 12 remains unexplained. However, on those two days the catalyst inlet elemental mercury concentrations were only about 2 μg/Nm^3. This made it necessary to measure catalyst outlet mercury concentrations of less than 1 μg/Nm^3 to be able to quantify high mercury oxidation efficiencies. The Hg SCEM being used at that time could not reliably quantify concentrations below 1 μg/Nm^3, so it is possible that this observed poor performance is due strictly to measurement challenges at these low concentration.

The next set of measurements was made in February 2004. The results are summarized in Table 4-36. The baghouse was rebagged starting in January. The measurements in February reflected operation with new bags in 11 of the 14 compartments in the west baghouse that treats flue gas going to the catalyst pilot unit. The results in Table 4-36 show that the partial rebagging had not markedly changed the mercury oxidation percentage at the baghouse outlet, since the February 13 measurements at the catalyst pilot inlet still showed 76% total mercury oxidation. This observation ruled out a previous theory that the high oxidation seen across this baghouse was due to metals (e.g., vanadium) in the permanent dustcake on the bags from previous co-firing of petroleum coke in the Spruce unit.

Table 4-35
December 2003 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Total Hg Adsorption Across Catalyst (%)	Apparent Hg^0 Oxidation Across Catalyst (%)	Overall Hg Oxidation Percentage
Results from 12/10/03:					
Pilot Inlet	11.7	4.1	-	-	65
C #6 Outlet	8.2	1.25	29	69	85
Au Outlet	6.6	0.90	43	76	85
Results from 12/11/03:					
Pilot Inlet	12.5	2.2	-	-	83
C #6 Outlet	15.2	1.31	0	40	91
Au Outlet	11.6	0.90	8	53	91
Results from 12/12/03:					
Pilot Inlet	14.6	1.65	-	-	89
Pd #1 Outlet	12.9	0.82	11	50	94
SCR Catalyst Outlet	17.0	0.74	0	55	96

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

Table 4-36
February 2004 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Total Hg Adsorption Across Catalyst (%)	Apparent Hg^0 Oxidation Across Catalyst (%)	Overall Hg Oxidation Percentage
Results from 2/13/04:					
Pilot Inlet	11.6	2.76	-	-	76
Pd #1 Outlet	12.2	1.13	0	59	91
C #6 Outlet	12.2	2.26	0	18	81
Au Outlet	12.4	0.68	0	76	95
SCR Catalyst Outlet	13.3	0.69	0	75	95

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

The February results show continuing variability in measured catalyst activity. The Pd #1 catalyst performance was similar to what was measured in December, but well below the initial activity in September. The C #6 catalyst showed a continuing decrease in performance from the December 11 results. The gold catalyst showed similar performance to what was measured December 10, and better performance than was measured December 11. Finally, the SCR catalyst showed better performance than was measured for that catalyst on December 12.

Measurement of catalyst activity at Spruce was difficult for two reasons. One is that because of mercury oxidation and capture across the baghouse, the elemental mercury concentrations at the oxidation catalyst pilot unit are relatively low, typically 3 $\mu g/Nm^3$ or lower. This means that for well performing catalysts, the catalyst outlet elemental mercury concentrations are on the order of 1 $\mu g/Nm^3$ or less, a low concentration that is difficult to measure accurately with the Hg SCEM (or by any other method). As described in Section 3 of this report, improvements to the Hg SCEM design while this project was in progress improved the ability to measure concentrations below 1 $\mu g/Nm^3$, although after the February 2004 measurements.

The second difficulty is that the pilot inlet total and elemental mercury concentrations are observed to change significantly throughout the day, apparently being impacted by factors such as baghouse pressure drop (fly ash buildup on the bags) and compartment cleaning cycles. This effect was previously discussed in Section 3. Significant temporal variations were seen during both the December and February measurements. A single Hg SCEM was being used to quantify catalyst performance and had to cycle between sampling the pilot inlet and the catalyst chamber outlet flue gases. Over this cycling period, inlet concentration variations can markedly impact observed mercury adsorption and elemental mercury oxidation percentages. As an example, on February 13, the pilot unit inlet elemental mercury concentration averaged 1.23 $\mu g/Nm^3$ at 10 a.m., but by 1:30 p.m. the average was 2.45 $\mu g/Nm^3$. This makes it difficult to determine what inlet value to use to calculate oxidation percentages for catalyst outlet elemental mercury concentrations measured between these two times. The latter value was used in Table 4-36 to calculate and report oxidation percentages across the catalysts.

Based on the February results, the gold and SCR catalysts were the most active, measured to be achieving approximately 75% elemental mercury oxidation. However, since the catalyst outlet mercury concentrations were less than 1 $\mu g/Nm^3$, this percentage cannot be stated with high precision. That is, the measurement precision at the value of 0.6 $\mu g/Nm^3$ seen at the outlets of these two catalysts is uncertain. The Pd #1 catalyst was achieving approximately 60% oxidation, and the C #6 catalyst only 20% oxidation. It is interesting that two better performing catalysts in the CCS pilot unit appeared to be poor performers at Spruce based on the February 2004 results.

The next catalyst activity measurement trip was conducted in May 2004. These results are shown in Table 4-37. As in all of the previous measurements, the pilot unit inlet showed high mercury oxidation percentages, with SCEM measurements showing 75% to 82% oxidized rather than the expected 20 to 30% oxidized mercury typical of PRB flue gases in plants that have ESPs for particulate control. The baghouse rebagging was complete by this time, so it appears that bag aging effects had not greatly influenced the previous mercury oxidation percentages measured across this baghouse. The baghouse outlet elemental mercury concentrations were measured to

range from 2.1 to 3.1 μg/Nm^3, which still were not as high as might be desired from the standpoint of accurately measuring oxidation catalyst performance.

Table 4-37
May 2004 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst (%)	Apparent Hg^0 Oxidation Across Catalyst (%)	Overall Hg Oxidation Percentage
Pd #1 Inlet	12.0	2.13	-	-	82
Pd #1 Outlet	11.2	0.14	7	94	99
C #6 Inlet	11.6	2.26	-	-	80
C #6 Outlet	11.6	0.21	0	91	98
Au Inlet	12.5	3.10	-	-	75
Au Outlet	11.8	0.24	5	92	98
SCR Catalyst Inlet	12.2	2.58	-	-	79
SCR Catalyst Outlet	12.6	0.15	0	94	99

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

Because of previous difficulties in measuring catalyst performance as described above, two Hg SCEMs were used during this trip, one dedicated to measuring inlet mercury concentrations while the other cycled through the four catalyst chamber outlets. URS' newest, highest resolution analyzer (at the time) was used for measuring the catalyst outlets, and increased measurement cycle times were employed so that the amount of mercury captured on the analyzer gold trap was above the low instrument calibration standard.

With this approach for measuring catalyst performance, it appeared that all of the catalysts were performing well, with each measuring greater than 90% oxidation and none adsorbing mercury in significant quantities. The data quality from this trip looked good - analyzer calibrations were consistent, spike recovery percentages were acceptable, and the cold vapor atomic absorption analyzers used in the SCEMs were producing sharp peaks with little noise apparent when the mercury desorbed.

The next set of catalyst measurement results was collected in August 2004. These results are shown in Table 4-38. As for previous trips, the measurements at the pilot unit inlet showed high mercury oxidation percentages, with SCEM measurements showing 87% to 90% oxidized mercury. The baghouse outlet elemental mercury concentrations were lower than were measured in May, averaging 1.25 μg/Nm^3.

Table 4-38
August 2004 Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Total Hg (μg/Nm^3, corrected to 3% O_2)*	Elemental Hg (μg/Nm^3, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst (%)	Apparent Hg^0 Oxidation Across Catalyst (%)	Overall Hg Oxidation Percentage
Pd #1 Inlet	9.66	1.25	-	-	87
Pd #1 Outlet	9.81	0.21	0	84	98
C #6 Inlet	11.3	1.25	-	-	89
C #6 Outlet	9.27	0.19	18	85	98
Au Inlet	12.4	1.25	-	-	90
Au Outlet	13.1	0.25	0	80	98
SCR Catalyst Inlet	12.4	1.25	-	-	90
SCR Catalyst Outlet	13.1	0.17	0	87	99

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

Because of equipment availability issues, a single Hg SCEM was used to quantify catalyst performance during this trip, and had to cycle between the pilot inlet flue gas sample and the catalyst chamber outlet samples, so inlet concentration variations could have impacted observed mercury adsorption and elemental mercury oxidation percentages. As during the May trip, a high resolution analyzer was used, and increased measurement cycle times were employed when sampling the catalyst outlets for elemental mercury, so the amount of mercury captured on the analyzer gold trap was above the low instrument calibration standard.

It appears that all of the catalysts were performing well in August. Each measured greater than 80% oxidation of elemental mercury. While this was down somewhat from what was measured in May (when all were measured at greater than 90% oxidation), the catalyst inlet elemental mercury concentration was considerably lower in August than in May. An average value of 1.25 μg/Nm^3 was measured in August while values ranging from 2 to 3 μg/Nm^3 were measured in May. For both measurement trips, the catalyst outlet elemental mercury concentrations were very similar, all in the range of 0.1 to 0.2 μg/Nm^3 corrected to 3% O_2 (~0.07 to 0.13 lb/10^{12} Btu heat input). It may be that these outlet concentrations represent the lower limit for the ability to measure low elemental mercury concentrations. If this were the case, the observed elemental mercury percentage oxidation across the catalysts subsequently would become a function of the inlet concentration rather than catalyst performance.

Only one catalyst, the C #6 catalyst, appeared to be adsorbing mercury in significant quantities in August. It was not clear why this would be occurring, because during the May measurements this catalyst appeared to be at adsorption equilibrium. Since only one analyzer was being cycled to

make these measurements, it is possible that the inlet flue gas total mercury concentration changed while the outlet flue gas from this catalyst was being sampled.

Results from the next catalyst activity measurement trip, in October 2004, are shown in Table 4-39. Measurements at the catalyst pilot unit inlet showed high mercury oxidation percentages, with SCEM measurements showing 60% to 80% oxidized mercury. Note that on this trip, the performance of each catalyst was measured on individual days, rather than all on a single day as on most previous measurement trips. These measurements were made with two Hg SCEMs.

Table 4-39
October Oxidation Catalyst Activity Results for Spruce Pilot (measured by Hg SCEM)

Location	Date	Total Hg ($\mu g/Nm^3$, corrected to 3% O_2)*	Elemental Hg ($\mu g/Nm^3$, corrected to 3% O_2)*	Apparent Total Hg Adsorption Across Catalyst (%)	Apparent Hg^0 Oxidation Across Catalyst (%)	Overall Hg Oxidation Percentage
Pd #1 Inlet	Oct. 19	10.7	2.7	-	-	75
Pd #1 Outlet	Oct. 19	12.1	0.6	0	76	95
C #6 Inlet	Oct. 21	13.8	3.4	-	-	75
C #6 Outlet	Oct. 21	10.4	0.7	24	80	94
Au Inlet	Oct. 20	9.7	3.9	-	-	60
Au Outlet	Oct. 20	10.0	0.3	0	92	97
SCR Catalyst Inlet	Oct. 22	8.1	1.6	-	-	80
SCR Catalyst Outlet	Oct. 22	9.1	1.0	0	41	89

*Note: 1.0 $\mu g/Nm^3$ at 3% O_2 equals 0.67 $lb/10^{12}$ Btu heat input

The day-to-day measurements summarized in Table 4-39 illustrate how variable the baghouse outlet/catalyst inlet total mercury and mercury oxidation were at Spruce Plant. Total mercury concentrations varied from 8.1 to 13.8 $\mu g/Nm^3$, and the mercury oxidation percentages varied from 60 to 80%. The resulting catalyst inlet elemental mercury concentrations varied by more than a factor of two, from 1.6 to 3.9 $\mu g/Nm^3$. During the previous catalyst activity measurements at Spruce in August, the mercury oxidation percentage at the baghouse outlet/catalyst inlet averaged an even higher value of 92%, and the inlet elemental mercury concentration was even lower at only 1.25 $\mu g/Nm^3$.

These variations are presumably due to variations in the coal mercury content, and/or baghouse operation. For example, baghouse cleaning cycles may impact baghouse outlet mercury concentration and speciation, as the “dirty” bags may adsorb and/or oxidize more mercury than just-cleaned bags, due to effects of the fly ash buildup on the bags. With the new bags in the baghouse, approximately eight hours elapse between cleaning cycles.

The October data suggest that the catalysts adsorb and desorb mercury as the inlet flue gas total mercury concentration varies. For example, on October 21 the inlet total mercury was measured at 13.8 μg/Nm^3, considerably higher than the value of 9.7 μg/Nm^3 measured the day before. On October 21, the catalyst outlet total mercury was measured to be lower than at the inlet, at 10.4 μg/Nm^3, indicating some mercury adsorption across the catalyst. The next day, the catalyst inlet total mercury was down to 8.1 μg/Nm^3, and the outlet was higher at 9.1 μg/Nm^3. This suggests that the catalyst was desorbing some of the mercury adsorbed the day before while treating flue gas with a significantly higher total mercury concentration. This effect is not surprising, since adsorption is typically a function of the partial pressure of the adsorbing species in the gas contacting the adsorbing solids, which is in turn a function of the absorbing species concentration in the gas.

These data also show an apparent correlation between catalyst inlet elemental mercury concentration and mercury oxidation percentage across the catalyst being evaluated. For example, the best performing, gold catalyst saw an inlet elemental mercury concentration of 3.9 μg/Nm^3, while the poorest performing, SCR catalyst saw an inlet concentration of only 1.6 μg/Nm^3. However, this appears to be only a coincidence, as such an effect was not seen in previous data, from May 2004, where two analyzers were also used to simultaneously measure the inlet and outlet elemental mercury concentrations for each catalyst.

The May through October data showed that three of the four catalysts were achieving greater than 75% oxidation of the inlet elemental mercury. The October data showed a significant drop in mercury oxidation activity for the fourth catalyst, the SCR catalyst, which was down to 41% oxidation across the catalyst from nearly 87% in August. The data for two other catalysts, the Pd #1 and C #6, showed a linear downward trend in measured activity over the time period of May through October. Only the gold catalyst data showed no tendency for loss of activity versus time, with the October data equaling the performance measured in May and improving over the performance measured in August.

The next catalyst measurement trip, in February 2005, was expected to produce the final set of catalyst activity measurements, as all of the catalysts had seen over 14 months of continuous operation in the Spruce flue gas. Measurements were made February 3rd and 4th, then again on February 7th through 10th. As during all of the previous measurement trips, these results showed that the baghouse outlet flue gas mercury content was highly oxidized, greater than 90% in some instances. This resulted in relatively low inlet elemental mercury concentrations to the pilot unit, often 1 μg/Nm^3 or less.

As for the May and October 2004 measurement trips, to improve the accuracy of the mercury oxidation measurements, two newer mercury SCEMs with more sensitive atomic absorption detectors were used to simultaneously monitor the pilot inlet and catalyst outlet locations. In spite of this measurement approach, the results from this trip were inconclusive with regards to oxidation catalyst activity for the four catalysts. In some cases, catalyst outlet total and/or elemental mercury concentrations were measured to be higher than inlet concentrations, which is not an expected result.

In view of these results, a number of quality control/quality assurance measures were implemented, in addition to routine analyzer calibrations and mercury spike recovery measurements. Additional measures included replacing a suspect mercury SCEM with a third unit, switching SCEM units between analyzing the catalyst inlet and catalyst outlet gas locations, and using temporary sample delivery piping and inertial gas separator (IGS) filters as a check on the permanently installed system.

None of these efforts conclusively improved the apparent quality of most of the measured mercury concentration data. For example, at times the two SCEMs were used to analyze the same species (total or elemental mercury) in flue gas from the same location (e.g., catalyst pilot inlet) through the two sample delivery systems. In some cases the results from the two analyzers and sample delivery systems agreed well, but in other instances there was a significant bias between the two analyzers' results. No consistent bias could be identified between the SCEMs in service or the sample conditioning and delivery systems, though.

Because of these measurement anomalies, most of the data from the February trip are not being presented in this report. A limited amount of data for the C #6 catalyst are reported below, though.

Spruce Plant was off-line for a spring outage from the week of February 21 through mid-March, 2005. The final catalyst measurement trip was conducted April 20-22, 2005. The pilot unit had been re-started on flue gas operation on March 29 following the outage, so the catalyst had seen over three weeks of flue gas service since being off line for a month. Overall, the Pd #1 and gold catalysts had seen about 17 months of flue gas service, and the C #6 and SCR catalysts had seen 16 months.

Because of the measurement issues in February, a number of extra quality assurance/quality control measures were implemented during the April trip. One was to sample the catalyst pilot unit inlet flue gas via two separate sample trains. One train used the normal, permanently installed tubing manifold, solenoid valves, inertial gas separator (IGS) filter and blower that were used to sample the pilot unit inlet and the outlets of each of the four catalysts throughout the project duration. The other train used a temporary piping, IGS and blower installation on a 4-in. port on the pilot unit inlet duct. The two measurement trains tracked changes in inlet total and elemental mercury concentrations over time very well, but the absolute values measured did not always agree well. The measured inlet flue gas elemental mercury concentrations were relatively low, though (1-2 $\mu g/Nm^3$), by either sampling system, which exacerbated the difficulty of getting good agreement between two independent measurements.

For this reason, it was decided to report the catalyst oxidation performance based on the train sampling the inlet flue gas through the permanent manifold assembly, since the catalyst outlet values were also measured through this train. A negative aspect of this decision is that it did not allow simultaneous measurement of the catalyst inlet and outlet concentrations, since a common manifold is used. However, the negative aspects of not being able to sample simultaneously were minimized by measuring inlet flue gas concentrations immediately before and after sampling each catalyst outlet.

The results of these "end of test" activity measurements are summarized in Table 4-40. Because of an oversight in setting up the sample solenoid sequencing during this time period, no data were collected for the performance of the C #6 catalyst. Instead, data collected in February 2005 that appeared to have been of acceptable quality are shown in the table.

Table 4-40
April 2005 "End-of-Test" Catalyst Oxidation Activity Data

Catalyst	Catalyst Inlet Hg^0 ($\mu g/Nm^3$, corrected to 3% O_2)*	Catalyst Outlet Hg^0 ($\mu g/Nm^3$, corrected to 3% O_2)*	Observed Hg^0 Oxidation Across Catalyst (%)
Pd #1	1.32	0.64	51
C #6	1.26**	1.18**	6**
Au	1.48	0.78	47
SCR	0.80	0.56	29

*Note: 1.0 $\mu g/Nm^3$ at 3% O_2 equals 0.67 $lb/10^{12}$ Btu heat input
**Data collected February 2005

The data in Table 4-40 show that the Pd and Au catalysts were each achieving approximately 50% elemental mercury oxidation, while the SCR catalyst was achieving about 30%. The February data show that the C #6 catalyst was achieving less than 10% oxidation.

Because considerable effort was expended trying to get high-quality data for catalyst inlet and outlet elemental mercury concentrations, only two of the catalysts were checked for total mercury breakthrough (Pd #1 and gold). These data are summarized in Table 4-41.

Table 4-41
April 2005 "End-of-Test" Catalyst Mercury Breakthrough Data

Catalyst	Catalyst Inlet Total Hg ($\mu g/Nm^3$, corrected to 3% O_2)*	Catalyst Outlet Total Hg ($\mu g/Nm^3$, corrected to 3% O_2)*	Observed Total Hg Breakthrough Across Catalyst (%)
Pd #1	11.0	12.7	116
C #6	**	**	**
Au	11.0	10.2	93
SCR	**	**	**

*Note: 1.0 $\mu g/Nm^3$ at 3% O_2 equals 0.67 $lb/10^{12}$ Btu heat input
**Not measured

It was expected that after the unit outage and exposure of the catalysts to ambient air, they would have desorbed some mercury and might have taken a few days to re-equilibrate. The results in Table 4-41 show that these two catalysts had achieved a high percentage mercury breakthrough

in the three weeks they had been in service following the unit outage, indicating that they were no longer adsorbing an appreciable amount of mercury from the inlet flue gas.

The activity data presented above in Tables 4-34 through 4-40 were used to generate a plot of measured catalyst activity versus time for the four catalysts in service at Spruce. This plot is shown in Figure 4-23. The data do not show a consistent trend for activity versus time in flue gas service. Only for the Pd #1 catalyst is there an apparent linear decrease in activity over time, but that is only for the time period May 2004 through April 2005 (shown as a dashed line on the figure). The data prior to May 2004 do not fit this apparent linear relationship, and there are earlier data that showed lower activity than even the "end of test" data.

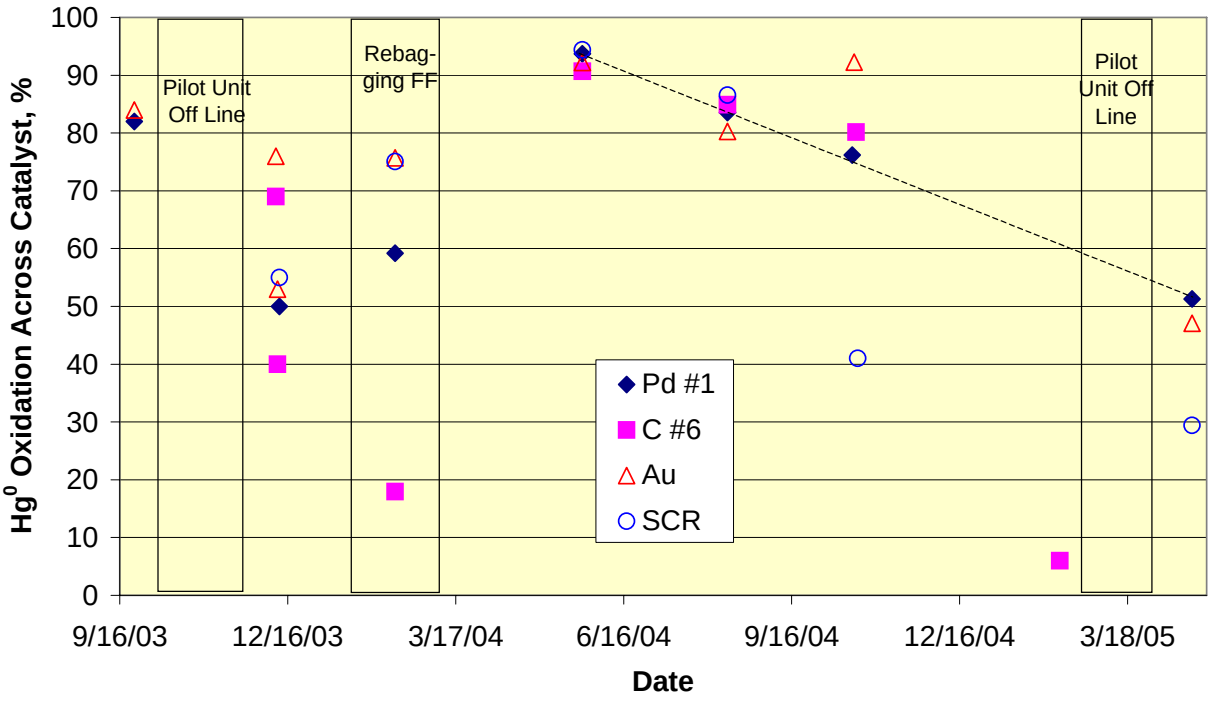

Figure 4-23
Spruce Catalyst Activity Data versus Time in Service

For the gold and C #6 catalysts, the end-of-test data show considerably lower performance than was expected based on the trends seen in the data collected between May and October 2004. In the May through October data, the C #6 catalyst mercury oxidation performance had been in the same range as the performance of the gold and palladium catalysts. However, in the end-of-test results, the C #6 catalyst performance was significantly below that of either the gold or palladium. The SCR catalyst end-of-test data were consistent with the significant drop in activity seen in the October 2004 data.

Given the difficulties in measuring catalyst performance in February and April 2005, and the extremely low and variable catalyst inlet elemental mercury concentrations, there was even some question as to whether these end of test performance values truly represent a loss of catalyst

activity, or whether the catalyst outlet elemental mercury concentrations were just too low to reliably measure by SCEM. Catalyst thermal regeneration tests were conducted the week of April 25, and the results of those tests are presented below. They indicate that the end of test values do represent activity losses that could be recovered by thermal regeneration.

Spruce Catalyst Regeneration Test Results

Catalyst thermal regeneration tests were conducted at Spruce the week of April 25, 2005. The tests were conducted by heating plant air with a 36-kW electric heater, then introducing the heated air through an existing port in the catalyst inlet transition (a port intended for sonic horns). Each catalyst was regenerated individually, and the intent was to isolate the catalyst chamber from inlet flue gas flow so that only heated air flowed over the catalyst. However, in actual practice there was some flue gas leakage through the catalysts as well. Each catalyst regeneration test was run from one morning to the next, with over 20 hours of elapsed time during the regeneration.

The regenerator was rebuilt from the one used previously at CCS, which had failed due to corrosion and wear and tear from being moved several times. The rebuilt regenerator was made to sit beside the catalyst pilot unit rather than bolt directly to the port on the catalyst inlet transition. While this reduced wear and tear on the regenerator associated with moving it, the fact that the heated air had to be ducted from the regenerator to the port on the catalyst box resulted in heat losses that limited the regeneration temperature achieved. The maximum regeneration temperature achieved at the catalyst outlet thermocouple for the Spruce regeneration tests was approximately 350 to 360^{o}F (177-182^{o}C), whereas in the Coal Creek regeneration tests the maximum temperatures were between 400 and 410^{o}F (204-210^{o}C). The temperature of the heated air entering the catalyst chamber was estimated to be between 500^{o}F and 600^{o}F (260-316^{o}C). In spite of the lower temperatures achieved, all four catalysts appeared to significantly improve in elemental mercury oxidation activity after regeneration. Trend plots showing the regeneration temperature, regeneration air flow rate, and total mercury concentrations measured in the catalyst outlet regeneration air are shown in Figures 4-24 through 4-27.

Mercury concentrations in the outlet air were measured as an indicator for how effectively species that had been adsorbed from the flue gas over time were desorbed during regeneration. Of course, the actual species that cause a loss of activity in the catalysts have not been identified to date, so it is not known what conditions are required to desorb these species relative to what is required to desorb mercury. It is hoped that further investigation of catalyst regeneration as part of a subsequent DOE NETL Cooperative Agreement (DE-FC26-04NT41992) will identify the species that cause loss of activity. Measurements conducted as part of a previous project suggested that selenium and or SO_3 may play a role.[2]

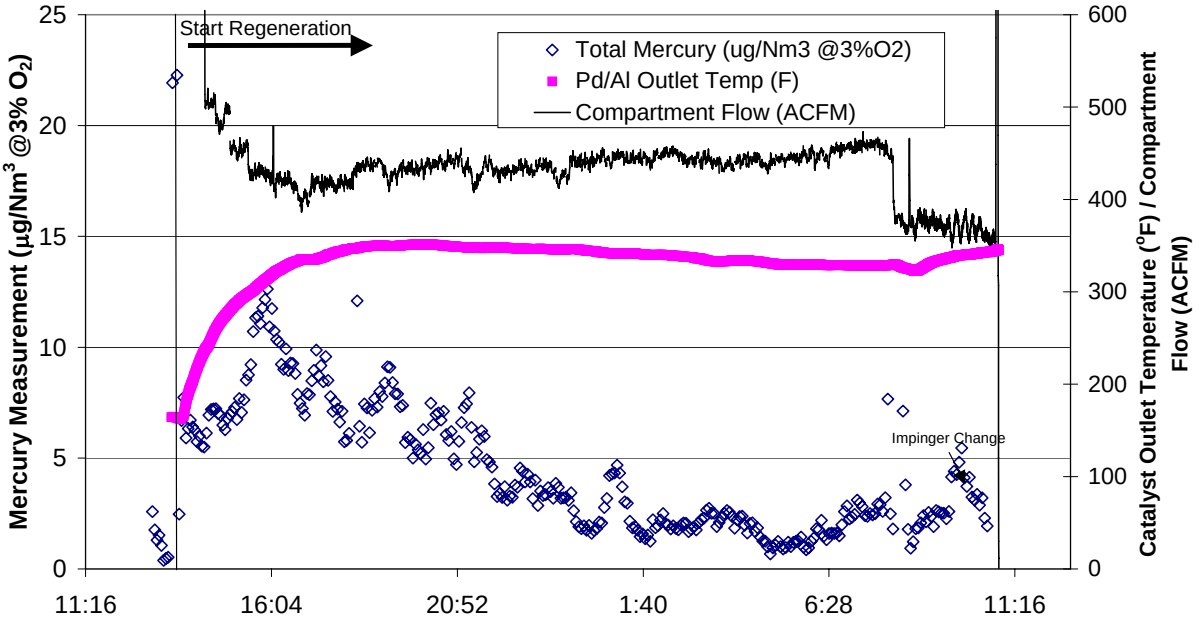

Figure 4-24
Trend Plot for Regeneration of the Pd #1 Catalyst

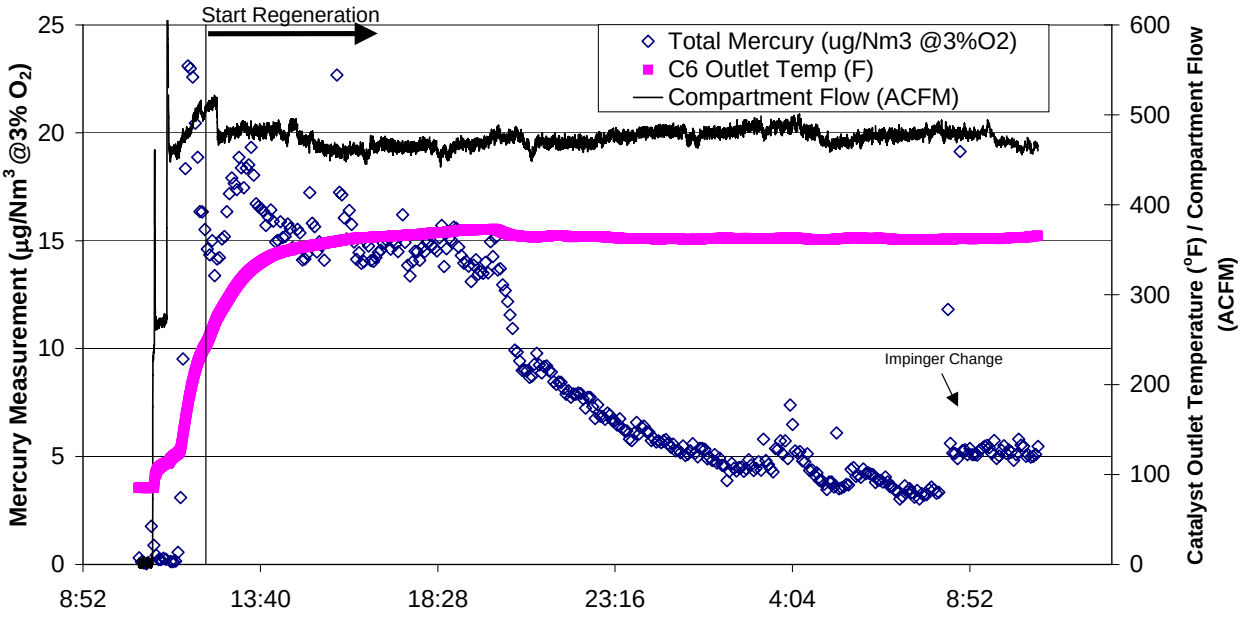

Figure 4-25
Trend Plot for Regeneration of the C #6 Catalyst

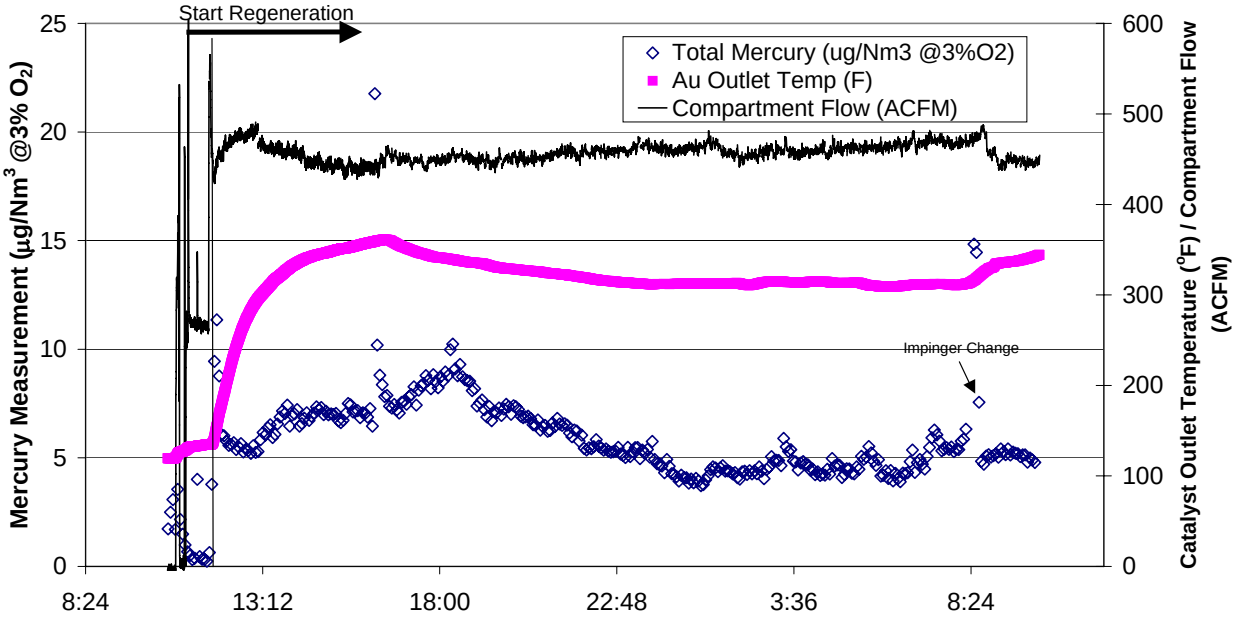

Figure 4-26
Trend Plot for Regeneration of the Gold Catalyst

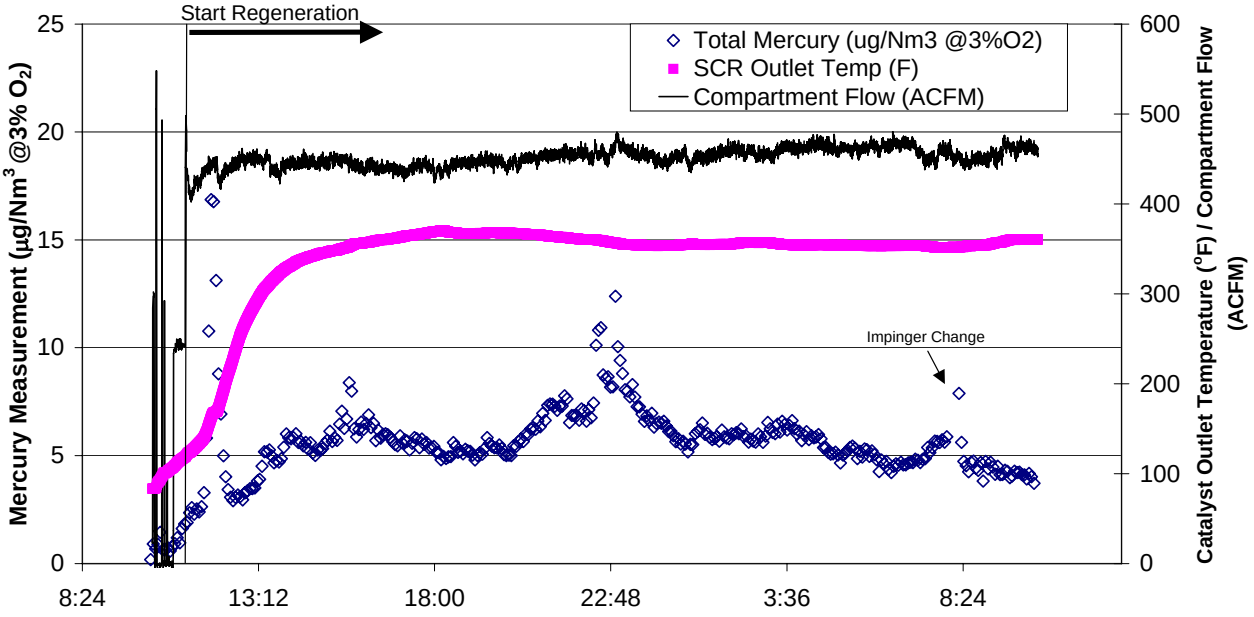

Figure 4-27
Trend Plot for Regeneration of the SCR Catalyst

The results plotted in the figures show that only for the Pd catalyst did the outlet mercury concentration peak and then return to near zero concentration (~2 µg/Nm^3 or less). The C #6 and

gold catalyst outlet regeneration air mercury concentrations peaked early in the regeneration, but stayed near 5 μg/Nm^3 after the overnight regeneration. The outlet air from the SCR catalyst regeneration slowly increased to about 5-6 μg/Nm^3 at the beginning of the regeneration and stayed near that value for the whole regeneration period, other than one brief increase about 12 hours into the regeneration. Based on the mercury concentration data alone, we would speculate that the Pd catalyst was most effectively regenerated at this temperature and duration. As discussed below, the Pd catalyst did prove to be the most active after regeneration.

The activity data for the regenerated catalysts are shown in Tables 4-42 and 4-43. As mentioned above, the Pd catalyst was the most active after regeneration, increasing from 51% elemental mercury oxidation prior to regeneration to 84% afterward. The gold catalyst saw nearly as great an improvement, going from 47% oxidation to 78%. The other two catalysts, which were considerably less active prior to regeneration, also saw substantial improvements in activity. The C #6 catalyst improved from less than 10% oxidation to 56%, while the SCR catalyst improved from 29% to 66%.

Table 4-42
May 2005 Post-regeneration Catalyst Oxidation Activity Data

Catalyst	Catalyst Inlet Hg^0 (μg/Nm^3 corrected to 3% O_2)*	Catalyst Outlet Hg^0 (μg/Nm^3 corrected to 3% O_2)*	Observed Hg^0 Oxidation Across Catalyst (%)
Pd #1	1.17	0.19	84
C #6	0.94	0.41	56
Au	0.88	0.19	78
SCR	0.90	0.30	66

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

Table 4-43
May 2005 Post-regeneration Catalyst Mercury Breakthrough Data

Catalyst	Catalyst Inlet Total Hg (μg/Nm^3 corrected to 3% O_2)*	Catalyst Outlet Total Hg (μg/Nm^3 corrected to 3% O_2)*	Observed Total Hg Breakthrough Across Catalyst (%)
Pd #1 (a.m. data)	5.3	5.9	110
Pd #1 (p.m. data)	10.1	9.7	96
C #6	10.4	8.9	85
Au	10.6	10.3	98
SCR	10.8	10.2	94

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

The regenerated catalysts were operated in their normal flue gas environment over a weekend prior to making these activity measurements the week of May 2nd. Total mercury concentration data summarized in Table 4-43 show that all of the catalysts were close to mercury adsorption equilibrium when these performance data were collected.

Spruce Flue Gas Characterization Results

Part of the long-term oxidation catalyst pilot test effort at Spruce Plant included characterizing the flue gas treated by the pilot unit. Over the 17 months of long-term catalyst testing, several flue gas characterization efforts were conducted. The measurements included:

- Pilot unit inlet and catalyst outlet mercury concentrations by the draft Ontario Hydro method (two times),
- Pilot unit inlet metals by Method 29,
- Pilot unit inlet halogens by Method 26a,
- Pilot unit inlet and catalyst outlet sulfuric acid by the Controlled Condensation method, and
- Full-scale baghouse and FGD module inlet and outlet mercury concentrations by Hg SCEM.

These results are presented and discussed in the following paragraphs.

Ontario Hydro Results – December 2003

During catalyst activity measurements the week of December 8, 2003, SCEM relative accuracy measurements were made using the Ontario Hydro method at the pilot unit inlet and the outlets of each of the four catalyst chambers. Metco Environmental collected the gas samples, and URS analyzed the resulting impinger solutions for mercury content. Tables 4-44 and 4-45 present the Ontario Hydro measurement results, along with average Hg SCEM data collected during the same time period as each Ontario Hydro run, for measurements on December 11 and 12, respectively.

The tables also show the relative accuracy between the Ontario Hydro and Hg SCEM measurements, calculated as the SCEM result minus the Ontario Hydro result, with the difference being expressed as a percentage of the Ontario Hydro result. In general, the total mercury concentration measurements agreed well between the two techniques, with the three-run average relative accuracy values ranging from –17% to +11%. The oxidized mercury concentration values also agree reasonably well between the two methods, with the average relative accuracy values ranging from –22% to +7%.

Table 4-44
Summary of Ontario Hydro Results from Spruce Plant, December 11, 2003

Sample Location	Ontario Hydro Results (corrected to 3% O_2)						Hg SCEM Results (corrected to 3% O_2)					Relative Accuracy		
	%O_2 in Flue Gas	Hg Ox. ($\mu g/Nm^3$)	Hg^0 ($\mu g/Nm^3$)	Total Hg ($\mu g/Nm^3$)	Total Hg Oxidation (%)	Hg^0 Ox. Across Catalyst (%)	Hg Ox. ($\mu g/Nm^3$)	Hg^0 ($\mu g/Nm^3$)	Total Hg ($\mu g/Nm^3$)	Total Hg Oxidation (%)	Hg^0 Ox. Across Catalyst (%)	Hg Ox. (%)	Hg^0 (%)	Hg Total (%)
Pilot Inlet	5.8	12.7	1.29	14.0	91	-	10.7	1.32	12.0	89	-	-16	2	-14
	5.7	13.9	1.60	15.5	90	-	12.0	2.22	14.3	84	-	-13	39	-8
	5.8	9.86	0.70	10.6	93	-	9.65	1.61	11.3	86	-	-2	129	7
Average	5.8	12.2	1.20	13.4	91	-	10.8	1.71	12.5	86	-	-11	43	-6
C #6 Outlet	5.4	14.0	0.26	14.2	98	80	8.88	2.62	11.5	77	-99	-36	898	-19
	5.4	17.6	0.40	18.0	98	75	14.7	0.74	15.5	95	66	-16	85	-14
	5.8	10.7	0.38	11.1	97	46	16.4	0.59	17.0	97	64	53	55	53
Average	5.5	14.1	0.35	14.4	98	71	13.3	1.32	14.6	91	23	-5	279	1
Au Outlet	5.6	14.3	0.16	14.4	99	88	10.4	1.23	11.6	89	7	-27	675	-19
	5.6	15.3	0.51	15.8	97	68	12.2	1.37	13.6	90	38	-20	170	-14
	5.8	11.2	0.26	11.5	98	63	9.04	0.45	9.49	95	72	-19	73	-17
Average	5.7	13.6	0.31	13.9	98	74	10.5	1.02	11.6	91	41	-22	229	-17

*Note: 1.0 $\mu g/Nm^3$ at 3% O_2 equals 0.67 $lb/10^{12}$ Btu heat input

Table 4-45
Summary of Ontario Hydro Results from Spruce Plant, December 12, 2003

Sample Location	Ontario Hydro Results (corrected to 3% O_2)*						Hg SCEM Results (corrected to 3% O_2)*					Relative Accuracy		
	%O_2 in Flue Gas	Hg Ox. ($\mu g/Nm^3$)	Hg^0 ($\mu g/Nm^3$)	Total Hg ($\mu g/Nm^3$)	Total Hg Oxidation (%)	Hg^0 Ox. Across Catalyst (%)	Hg Ox. ($\mu g/Nm^3$)	Hg^0 ($\mu g/Nm^3$)	Total Hg ($\mu g/Nm^3$)	Total Hg Oxidation (%)	Hg^0 Ox. Across Catalyst (%)	Hg Ox. (%)	Hg^0 (%)	Hg Total (%)
Pilot Inlet	5.8	11.2	0.16	11.4	99	-	8.35	3.87	12.2	68	-	-25	2270	8
	5.4	11.9	0.52	12.4	96	-	9.74	1.43	11.2	87	-	-18	176	-10
	5.4	11.3	0.60	11.9	95	-	15.4	0.88	16.3	95	-	36	47	37
Average	5.5	11.5	0.43	11.9	96	-	11.2	2.06	13.2	84	-	-3	383	11
Pd #1 Outlet	6.0	12.6	0.39	13.0	97	-141	10.2	1.58	11.8	87	59	-19	300	-9
	6.0	13.9	0.40	14.3	97	22	11.2	0.78	12.0	94	46	-19	92	-16
	5.4	12.4	0.41	12.8	97	31	16.3	0.23	16.6	99	74	32	-45	30
Average	5.8	12.9	0.40	13.3	97	5	12.6	0.86	13.5	94	58	-3	113	1
SCR Outlet	6.0	15.9	0.28	16.1	98	-69	12.4	1.28	13.7	91	67	-22	365	-15
	5.6	13.6	0.34	13.9	98	34	15.2	0.77	15.9	95	46	12	124	15
	5.4	12.7	0.33	13.0	97	45	17.4	0.18	17.6	99	79	37	-46	35
Average	5.7	14.0	0.32	14.4	98	26	15.0	0.74	15.7	95	64	7	135	9

*Note: 1.0 $\mu g/Nm^3$ at 3% O_2 equals 0.67 $lb/10^{12}$ Btu heat input

This is seen as very good agreement, especially given the observed temporal concentration variations in the flue gas during this time period. Although the reported Ontario Hydro and Hg SCEM data were collected over the same time periods, the Ontario Hydro measurements represent time averaged values over two hours, whereas the Hg SCEM values represent an average over only a subset of time during that two hours. A single Hg SCEM was cycled between the pilot inlet and two catalyst outlet sample locations, and between measuring total and elemental mercury during that two-hour period. Thus, there are only about 20 minutes of SCEM measurement data at each location and for each mercury species during the two-hour Ontario Hydro run.

The elemental mercury concentrations did not agree well between the two methods. The three-run-average relative accuracy values ranged from +43% to +383%, indicating that the Hg SCEM average values were higher than the Ontario Hydro average values by as much as a factor of four. A similar effect was seen in the SCEM relative accuracy tests conducted at CCS in July, 2003, as discussed earlier in this section. The individual run data show an even wider range of discrepancy between the methods, with individual relative accuracy values ranging from –46% to +2270%. It is not clear which, if either of the two methods more accurately reflects the amount of elemental mercury in the flue gas at Spruce, particularly for the catalyst outlet locations.

The Ontario Hydro elemental mercury values appear to be biased low. For example, the pilot unit average inlet mercury oxidation was measured at 96% on December 12, with individual runs showing 95 to 99% oxidation. Such high oxidation percentages do not seem plausible for a PRB flue gas, even with a baghouse upstream. Given the low inlet elemental mercury concentration measured by the Ontario Hydro Method on the 12th, it is not clear that the Pd #1 and SCR catalyst outlet elemental mercury concentration and catalyst oxidation percentage values shown in Table 4-45 represent measurable results.

There are also anomalies in the Hg SCEM results. For the four catalyst outlet locations and the pilot inlet location on one of the two days, there was an observed continual lowering of the elemental mercury concentration from the first through the third run periods. For these five measurement sets, the elemental mercury concentration measured on the first run at a particular location ranged from being three to seven times the value measured on the third run at that location. It does not seem plausible that elemental mercury concentrations would drop so markedly during the course of a day, and it seems more likely that these trends represent some type of undiagnosed measurement bias.

Because there was so much run-to-run variability in these results, they have been presented in an alternate manner in Table 4-46: as means and 95% confidence intervals of those means for the three runs of each type. When the 95% confidence intervals of the means are reviewed, it is apparent which means have the most uncertainty. In most cases, the apparent disagreement between the Ontario Hydro and SCEM results for elemental mercury concentrations can be explained by the high degree of uncertainty in the results, particularly by SCEM but in some instances in the Ontario Hydro results as well. As an example, the catalyst inlet measurements on December 12 showed a mean elemental mercury concentration of 0.43 $\mu g/Nm^3$ by Ontario Hydro, but the 95% confidence interval is ± 0.26 $\mu g/Nm^3$. The comparable SCEM results show a

mean inlet elemental mercury concentration of 2.1 μg/Nm^3, but the 95% confidence interval is ±1.8 μg/Nm^3. This means that we have a 95% certainty that the true mean value as measured by Ontario Hydro was in the range of 0.17 to 0.69 μg/Nm^3, while the true mean value as measured by SCEM was in the range of 0.3 to 3.9 μg/Nm^3. Since these two intervals overlap, it is possible that the poor relative accuracy between these two methods for this measurement is due to uncertainty in the means rather than a bias between the methods.

Table 4-46
December 2003 Ontario Hydro Relative Accuracy Results for Spruce Pilot (mean and 95% confidence interval of three runs, compared to Hg SCEM results from same time period)

	Total	**Elemental**	**Oxidized**
Catalyst Inlet, December 11, 2003			
Catalyst Inlet – OH, μg/Nm^3 corrected to 3% O_2*	13.4 ± 2.5	1.2 ± 0.5	12.2 ± 2.3
Catalyst Inlet - SCEM, μg/Nm^3 corrected to 3% O_2	12.5 ± 1.8	1.7 ± 0.5	10.8 ± 1.4
Relative Accuracy, % (based on means)	-6	43	-11
C #6, December 11, 2003			
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	14.4 ± 3.9	0.35 ± 0.08	14.1 ± 3.9
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	14.6 ± 3.2	1.3 ± 1.3	13.3 ± 4.5
Relative Accuracy, % (based on means)	1	279	-5
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	71 ± 20	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	23 ± 107	-
Gold, December 11, 2003			
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	13.9 ± 2.5	0.31 ± 0.20	13.6 ± 2.4
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	11.6 ± 2.3	1.0 ± 0.6	10.5 ± 1.8
Relative Accuracy, % (based on means)	-17	229	-22
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	74 ± 15	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	41 ± 37	-
Catalyst Inlet, December 12, 2003			
Catalyst Inlet – OH, μg/Nm^3 corrected to 3% O_2	11.9 ± 0.6	0.43 ± 0.26	11.5 ± 0.4
Catalyst Inlet - SCEM, μg/Nm^3 corrected to 3% O_2	13.2 ± 3.1	2.1 ± 1.8	11.2 ± 4.2
Relative Accuracy, % (based on means)	11	383	-3

Table 4-46 (Continued)

	Total	Elemental	Oxidized
Pd #1, December 12, 2003			
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	13.3 ± 0.9	0.40 ± 0.01	12.9 ± 0.9
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	13.5 ± 3.1	0.86 ± 0.77	12.6 ± 3.7
Relative Accuracy, % (based on means)	1	113	-3
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	5 ± 110	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	58 ± 16	-
SCR Catalyst, December 12, 2003			
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	14.4 ± 1.8	0.32 ± 0.04	14.0 ± 1.9
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	15.7 ± 2.2	0.74 ± 0.62	15.0 ± 2.8
Relative Accuracy, % (based on means)	9	135	7
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	26 ± 71	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	64 ± 19	-

*Note: 1.0 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

Ontario Hydro Results – October 2004

The week after catalyst activity tests were conducted on the oxidation catalyst pilot unit at Spruce in October 2004, a second week of testing was conducted, including Hg SCEM relative accuracy tests by the Ontario Hydro method. The results from the Ontario Hydro relative accuracy tests are summarized in Table 4-47. The data in Table 4-47 are presented in the same manner as in Table 4-46 above, showing mean and 95% confidence interval values.

The Hg SCEM results from this second week were not reported previously in Table 4-39 and Figure 4-23 for two reasons. One is that, because of sampling port configurations, it was not possible to sample the catalyst inlet and outlet locations simultaneously with two Hg SCEMs during the Ontario Hydro method sampling. As described previously, this makes any oxidation percentage measurements suspect because of the observed variability in total and elemental mercury concentrations at the Spruce baghouse outlet/oxidation catalyst pilot unit inlet.

The second reason the results from the second week were not included in the previous catalyst performance results tables is that during the second week, a heater on the IGS filter used to extract a particulate-free sample into the impinger train for the Hg SCEM failed. Although the sampling crew attempted to compensate for this failure by wrapping the IGS filter with heat tape

Table 4-47
October 2004 Ontario Hydro Relative Accuracy Results for Spruce Pilot (mean and 95% confidence interval of three runs, compared to Hg SCEM results from same time period)

	Total	Elemental	Oxidized
Pd #1, October 26, 2004			
Catalyst Inlet – OH, μg/Nm^3 corrected to 3% O_2*	5.0 ± 4.1	0.5 ± 0.1	4.5 ± 4.1
Catalyst Inlet - SCEM, μg/Nm^3 corrected to 3% O_2	6.0 ± 0.8	0.9 ± 0.8	5.3 ± **
Relative Accuracy, % (based on means)	20	80	18
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	5.7 ± 3.7	0.5 ± 0.2	5.2 ± 3.5
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	6.1 ± 2.3	0.6 ± 0.5	5.5 ± 1.8
Relative Accuracy, % (based on means)	7	18	6
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	7	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	39	-
C #6, October 28, 2004			
Catalyst Inlet - OH, μg/Nm^3 corrected to 3% O_2	9.1 ± 3.1	0.8 ± 0.5	8.3 ± 3.2
Catalyst Inlet - SCEM, μg/Nm^3 corrected to 3% O_2	8.4 ± 1.0	0.7 ± **	7.1 ± **
Relative Accuracy, % (based on means)	-8	-13	-15
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	10.4 ± 0.4	0.4 ± 0.4	10.0 ± 0.2
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	6.2 ± 0.1	1.1 ± 0.3	5.2 ± 0.2
Relative Accuracy, % (based on means)	-40	167	-48
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	50	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	-52	-

Table 4-47 (Continued)

	Total	Elemental	Oxidized
Gold, October 27, 2004			
Catalyst Inlet – OH, μg/Nm^3 corrected to 3% O_2	12.0 ± 1.7	3.0 ± 0.6	8.9 ± 1.2
Catalyst Inlet - SCEM, μg/Nm^3 corrected to 3% O_2	8.9 ± 3.2	2.7 ± 0.7	6.2 ± 3.2
Relative Accuracy, % (based on means)	-26	-11	-31
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	10.3 ± 3.1	0.4 ± 0.3	10.0 ± 2.8
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	10.9 ± 0.9	1.0 ± 0.4	10.0 ± 0.5
Relative Accuracy, % (based on means)	6	164	0
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	88	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	64	-
SCR Catalyst, October 29, 2004			
Catalyst Inlet – OH, μg/Nm^3 corrected to 3% O_2	7.9 ± 1.5	1.0 ± 0.8	6.9 ± 2.2
Catalyst Inlet - SCEM, μg/Nm^3 corrected to 3% O_2	7.2 ± 1.5	0.4 ± 0.0	6.4 ± 2.3
Relative Accuracy, % (based on means)	-9	-60	-8
Catalyst Outlet - OH, μg/Nm^3 corrected to 3% O_2	7.9 ± 2.4	0.2 ± 0.1	7.7 ± 2.4
Catalyst Outlet - SCEM, μg/Nm^3 corrected to 3% O_2	7.7 ± 1.5	0.6 ± 0.2	6.9 ± 2.6
Relative Accuracy, % (based on means)	-2	260	-11
Observed Hg^0 Oxidation Across Catalyst, % by OH	-	83	-
Observed Hg^0 Oxidation Across Catalyst, % by SCEM	-	50	-

*****Note: 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input
**Hg SCEM data were available for only one of the three OH runs, so 95% confidence interval could not be calculated

and insulation, the IGS filter temperature remained at about 270°F (132°C), which is well below the desired temperature of 400°F (204°C). Although the SCEM results from the second week do not show clear signs of measurement bias, they remain suspect.

As was seen the week before and reported previously in Table 4-39, the flue gas total and elemental mercury concentrations also varied considerably from day to day in the results presented in Table 4-47. As measured by the Ontario Hydro method, the catalyst pilot unit inlet total mercury concentrations varied from 5.0 to 12.0 μg/Nm^3, a factor of more than two. The inlet elemental mercury concentrations varied from 0.5 to 3.0 μg/Nm^3, a factor of six.

Because of the observed variability in concentrations, the table shows the mean value for three runs (sometimes fewer than three for the Hg SCEM as discussed below) as well as the 95% confidence interval of the mean. As discussed above for Table 4-46, the magnitude of the 95% confidence interval can be compared to the mean value to provide a measure of the variability of the measurements. The larger the 95% confidence interval relative to the mean value, the more variable were the measurement results. This variability could be due to changes in the actual flue gas concentrations over time, variability within the measurement methods, or both.

Since the Hg SCEM measurements were made with only one analyzer, this meant that four measurements had to be made (catalyst inlet and outlet, total and elemental mercury) while the two Ontario Hydro trains (catalyst inlet and outlet) completed each two-hour run. Thus, the Hg SCEM data for each of the four measurements represent, at best, 20 to 30 minutes of data collected at different times during the Ontario Hydro runs while the Ontario Hydro results represent an integrated sample collected over the entire two hours. Furthermore, because of the IGS filter heating issues discussed above, for some Ontario Hydro run periods, all four Hg SCEM measurements were not completed, as time was lost trying to get the IGS filter up to temperature. Since the oxidized mercury concentration is measured by the difference between total and elemental mercury with the Hg SCEM, this meant that any time either a total or elemental mercury concentration was not measured at a location, the oxidized mercury concentration could not be calculated either. Thus, for some Ontario Hydro mean values in Table 4-47, each of which represents three runs, the Hg SCEM data may only correspond with one or two of those Ontario Hydro runs. The ones with only one set of SCEM data are noted in the table with double asterisks, as a 95% confidence interval cannot be calculated from only one value.

Comparing the Ontario Hydro method results to Hg SCEM results, the catalyst inlet and outlet total mercury measurements agreed well for all but two sets of data: the catalyst inlet on October 27 (gold catalyst) and the catalyst outlet on October 28 (C #6 catalyst). In the case of the inlet on October 27, the disagreement may be due to the observed high variability of the inlet total mercury concentrations. When the 95% confidence intervals about the means for the two measurement methods are compared, they overlap considerably. For the outlet of the C #6 catalyst on October 28, there is apparently some bias between the two methods, as the 95% confidence intervals are relatively small for the mean values by both methods and the two 95% confidence intervals about the means do not come close to overlapping.

For the elemental mercury concentration measurements, the catalyst inlet concentration data agree reasonably well between the two methods, particularly when the 95% confidence intervals about the mean values are considered. On the days where the mean values differed significantly, the confidence intervals were large for one or more method, so the 95% confidence intervals for the means by the two methods overlapped in each case.

For the catalyst outlet elemental mercury measurements, a bias appears to be present in these results: in general, the Ontario Hydro method measures lower elemental mercury concentrations at the oxidation catalyst outlet locations than does the Hg SCEM. For some of the measurements, though, the apparent bias is within the 95% confidence intervals of the mean values for the two methods.

For oxidized mercury concentrations, the two methods agreed well except for the two measurements where the SCEM results for total mercury concentration appeared to be biased low relative to the Ontario Hydro results: the catalyst inlet on October 27 (gold catalyst) and the catalyst outlet on October 28 (C #6 catalyst). Since the SCEM measures oxidized mercury concentrations as the difference between the total and elemental mercury concentrations, this apparent bias was carried over to the oxidized mercury concentration by the SCEM method. As with the total mercury data, for the October 27 data the difference between the two methods may be explained by data variability (large 95% confidence intervals), but this is not the case for the October 28 data.

Table 4-47 also shows observed oxidation percentages across the catalysts. For three of the four days, the mean catalyst inlet elemental mercury concentrations were 1 $\mu g/Nm^3$ or lower. A number of the individual run results at the catalysts' inlets and outlets showed elemental mercury concentrations below 0.5 $\mu g/Nm^3$, the stated lower measurement limit of the Ontario Hydro Method.[5] Consequently, for the three catalysts tested on these days (Pd #1, C #6 and SCR) the Ontario Hydro results may not be valid. Based on past experience at Spruce, the Hg SCEM does not appear to be able to successfully measure catalyst oxidation performance when the inlet elemental mercury concentration is below 1 $\mu g/Nm^3$ either. The mean elemental mercury oxidation percentages across these three catalysts range from 18 to 83% by the Ontario Hydro Method and from –52 to +50% by Hg SCEM. None of these results is believed to be valid.

For the gold catalyst, the mean inlet elemental mercury concentration was about 3 $\mu g/Nm^3$, which should be high enough to allow measurement of catalyst performance. The mean percent oxidation across the gold catalyst by the Ontario Hydro method was 88%, which is in good agreement with the 92% value measured simultaneously with two Hg SCEMs the week before. The mean value for the Hg SCEM data for the gold catalyst was 64% oxidation, which is well below the 92% value measured the week before. However, as stated previously the Hg SCEM data in Table 4-46 were measured with only one analyzer, which makes catalyst performance measurement difficult due to observed variability in inlet flue gas elemental mercury concentrations. When the 95% confidence intervals of the Hg SCEM data are considered, the 95% confidence interval of the mean oxidation percentage calculated from those values ranges from 30% to 84%, the latter of which is near the performance measured the week before.

Flue Gas Metals (Method 29)

Additional flue gas characterization measurements were made at Spruce Plant in December 2003, including trace metals (EPA Method 29) at the pilot unit inlet. The Method 29 non-mercury metals results are presented in Table 4-48, while the mercury results are presented in Table 4-49. The data in both tables are discussed below.

As might be expected downstream of a well-performing baghouse, the metals concentration results in Table 4-48 show very little particulate-bound metals. Even in the vapor phase, metals concentrations were below measurable levels for all but aluminum, iron, tin and zinc. Note that the large difference in reported detection limits for the vapor phase antimony concentrations is due to differences in the sample dilution levels at which the laboratory chose to run these samples.

Table 4-48
Method 29 Data from Spruce Oxidation Catalyst Pilot Unit Inlet, 9 December 2003 (all values shown in ppbv (dry basis), particulate values shown as equivalent gas-phase concentration)

	Gas Phase Measurement Results				**Particulate Phase Measurement Results**			
	Run 1	**Run 2**	**Run 3**	**Average**	**Run 1**	**Run 2**	**Run 3**	**Average**
Start Time	9:05	11:40	14:15	**-**	9:05	11:40	14:15	**-**
Aluminum	5,416	23,243	14,357	**14,339**	128	54	234	**139**
Antimony	<542	<536	<5,495	**<2,191**	ND	ND	ND	**ND**
Arsenic	ND	ND	ND	**ND**	ND	ND	ND	**ND**
Barium	<3,620	<3,586	<3,598	**<3,601**	0.72	1.2	46.0	**16.0**
Beryllium	ND	ND	ND	**ND**	ND	ND	ND	**ND**
Cadmium	<111	<110	<110	**<110**	0.03	<0.09	<0.09	**<0.07**
Calcium	<310,053	<307,159	<308,247	**<308,486**	126	92	71	**96.4**
Chromium	<478	<474	<475	**<475**	0.45	*	*	**-**
Cobalt	<2107	<209	<210	**<842**	<1.7	<1.8	<1.7	**<1.7**
Copper	<977	<969	<972	**<973**	0.37	*	*	**-**
Iron	ND	2645	4867	**3756**	9.4	7.7	24.2	**13.8**
Lead	<120	<119	<119	**<119**	<0.10	<0.10	<0.10	**<0.10**
Magnesium	<510,785	<506,414	<508,208	**<508,469**	<416	<426	<417	**<419**
Manganese	<678	<672	<675	**<675**	0.58	0.42	1.02	**0.67**
Molybdenum	ND	ND	ND	**ND**	0.11	0.00	0.02	**0.04**
Nickel	<1,693	<1,678	<1,684	**<1,685**	<1.4	<1.4	<1.4	**<1.4**
Potassium	-	-	-	**-**	<259	<265	<259	**<261**
Selenium	283	<312	<313	**<303**	ND	ND	ND	**ND**
Silver	<629	<78	<78	**<262**	ND	ND	ND	**ND**
Sodium	-	-	-	**-**	290	*	467	**-**
Thallium	ND	ND	ND	**ND**	ND	ND	ND	**ND**

Table 4-48 (Continued)

	Gas Phase Measurement Results				Particulate Phase Measurement Results			
	Run 1	**Run 2**	**Run 3**	**Average**	**Run 1**	**Run 2**	**Run 3**	**Average**
Tin	1,883	2,074	12,074	**5,344**	<1.7	<1.7	<1.7	**<1.7**
Titanium	<2,594	<2,572	<2,581	**<2,582**	1.6	1.5	2.6	**1.9**
Vanadium	ND	ND	ND	**ND**	ND	ND	ND	**ND**
Zinc	1,747	1,694	38	**1,160**	6.0	0.6	*	**-**

*Value measured was less than field blank value

Table 4-49
Method 29 Mercury Data from Spruce Oxidation Catalyst Pilot Unit Inlet, 9 December 2003 (all values shown in μg/Nm^3, particulate values shown as equivalent gas-phase concentration)

	Particulate Phase Hg, μg/Nm^3 corrected to 3% O_2*	M29 Gas Phase Hg, μg/Nm^3 corrected to 3% O_2*	SCEM Gas Phase Hg, μg/Nm^3 corrected to 3% O_2*	Relative Accuracy, %
Run 1	0.01	15.9	-	-
Run 2	0.00	14.6	14.3	-2
Run 3	0.01	14.4	11.2	-23
Average	0.01	15.0	-	-

*****Note: 1 μg/Nm^3 at 3% O_2 equals 0.67 lb/10^{12} Btu heat input

The Method 29 mercury concentrations are compared to mercury SCEM values in Table 4-49. SCEM data were not available for the first Method 29 run. For the second run, the relative accuracy between the two methods was very good, with the SCEM value being 2% lower than the Method 29 value. For the third run, the difference was greater, with the SCEM value being 23% lower.

Flue Gas Halogen Species (Method 26a)

Three Method 26a runs were conducted at the Spruce catalyst pilot inlet flue gas location in December 2003. Each showed pilot unit inlet HCl concentrations of 0.8 ppmv (dry basis), and Cl_2 concentrations of <0.02 ppmv (dry basis).

Flue Gas Sulfuric Acid Concentrations (Controlled Condensation Method)

In December 2003, three Controlled Condensation method runs were conducted at the Spruce catalyst pilot inlet flue gas location and at the outlets of two of the catalysts. The runs showed very low sulfuric acid vapor concentrations at the pilot inlet and at the outlets of both the C #6 and gold catalysts. All measured values were less than 0.1 ppmv of H_2SO_4 (dry basis).

Other Flue Gas Characterization Results

Another type of gas characterization effort was conducted at Spruce, the first week of January 2004. URS set up two Hg SCEMs on the host unit ductwork, one on the outlet duct of one wet FGD absorber and one alternated between the baghouse outlet and inlet ducts. The objective of these measurements was to characterize the mercury oxidation and removal across the baghouse with the existing, aged bags prior to the rebagging effort, which was to begin the next week. The FGD outlet measurements were made to confirm that the mercury being oxidized across the baghouse was, in fact, being removed by the wet FGD system at high efficiency. At the same time, CPS Energy had contracted with Metco Environmental to collect stack gas metals concentration data by Method 29, so this provided an opportunity to compare SCEM results to reference method results for flue gas mercury concentration.

The Hg SCEM results are summarized in Table 4-50. The results show very high oxidation percentages across the baghouse, but less mercury removal across the wet FGD absorber than expected.

Table 4-50
Mercury Concentration Data at Spruce by Hg SCEM, January 2004

Location	Hg Concentration ($\mu g/Nm^3$ corrected to 3% O_2)*			Overall Hg Oxidation (%)	Hg Removal Relative to Baghouse Inlet (%)	Hg Ox. Across Baghouse (%)	Hg Removal Across FGD Absorber (%)		
	Hg Total	Hg^0	Hg^{+2}				Hg Total	Hg^0	Hg^{+2}
Baghouse Inlet (7-Jan)	15.2	12.8	2.46	16	-	-	-	-	-
Baghouse Outlet (6-Jan)	14.3	0.85	13.5	94	6**	93**	-	-	-
FGD Outlet (6-Jan)	5.38	-	-	-	65**	-	62		
FGD Outlet (7-Jan)	3.62	1.52	2.11	58	76	-	75**	-78**	84**

* Note: 1 $\mu g/Nm^3$ at 3% O_2 equals 0.67 $lb/10^{12}$ Btu heat input
**Percentage was calculated using inlet data from previous or following day, so the value shown may be biased by day-to-day variability

Unfortunately, some potentially useful measurements were not made at the time. No elemental mercury numbers were measured for the FGD outlet on January 6. Since Method 29 does not speciate mercury, the engineer running that analyzer concentrated on measuring only total mercury numbers for comparison. On the 7th the procedure was changed to measure both total

and elemental mercury concentrations with the FGD outlet analyzer. Since only two analyzers were used, baghouse outlet data were collected the first day and inlet data the second. Therefore, there are unfortunately no baghouse outlet speciation data for the 7th, the only day FGD outlet speciation data are available.

Consequently, there is not a direct measure of elemental mercury "re-emissions" across the scrubber. Based on the baghouse outlet for January 6 and the scrubber outlet for January 7, a small amount of elemental mercury re-emissions is evident. However, since the two measurements are on different days and given the amount of variation previously and subsequently measured in elemental mercury concentrations at this site, this cannot be considered conclusive evidence of mercury re-emissions.

The data in Table 4-50 show 84% removal of oxidized mercury across the FGD absorber, although this percentage is based on an FGD inlet oxidized mercury concentration measured the day before. This is a lower oxidized removal percentage than would be expected. The SO_2 removal across the FGD system at Spruce was about 92% at the time. One would expect similar or greater removal percentages for oxidized mercury, in the absence of re-emissions. The FGD inlet oxidized mercury concentration to the FGD system would have had to be greater than 21 $\mu g/Nm^3$ on January 7 for the actual oxidized mercury removal across the FGD absorber to have been above 90%, and such a concentration is above the range previously measured at Spruce. This consideration further supports the observation that there was a small amount of mercury re-emissions across the FGD system at Spruce.

CPS Energy also reported the stack total mercury concentrations measured at Spruce by Metco Environmental by Method 29 (M29). For January 7, the stack and FGD outlet total mercury concentrations measured by SCEM should have been equivalent, as the FGD system was being operated with no flue gas bypass. On January 6, the FGD bypass damper was partially open and about 15 to 20% of the baghouse outlet gas was bypassing the FGD system. Thus, the M29 results for the stack gas should have shown higher total mercury concentrations than the Hg SCEM results at the baghouse outlet. A comparison between the two sets of measurements is shown in Table 4-51.

The four columns of information on the right in the table were used to estimate the stack total mercury concentration from the Hg SCEM data. SCEM data from the baghouse outlet and FGD outlet were weighted based on a bypass percentage estimated from stack flue gas temperature.

The ability to compare the results of these two methods is confounded by the relatively high detection limits for mercury shown in the M29 results. The comparison in the table shows that the M29 measurements on January 6 were lower than were measured with the SCEM, while the data from January 7 show reasonable agreement.

Table 4-51
Comparison of Stack M29 Data and Hg SCEM Data from FGD Outlet

Date	Time	Run	M29 Results at Stack (Hg, μg/Nm^3 @ 3% O_2)	Hg SECM Results at FGD Outlet (Hg, μg/Nm^3 @ 3% O_2)	Stack Temp (^{o}F)	Hg SCEM Results at FF Outlet (Hg, μg/Nm^3 @ 3% O_2)	Estimated % Gas Bypass	Estimated Hg SCEM Results at Stack (Hg, μg/Nm^3 @ 3% O_2)
6-Jan	0945-1205	1	5.86	5.18	153	15.0	14%	6.6
6-Jan	1323-1546	2	4.93	6.42	156	14.8	16%	7.8
Average			5.39	5.80	155	14.9	15%	7.2
7-Jan	0800-1022	1	2.91	4.75	132	-	0%	4.75
7-Jan	1110-1336	2	3.95	2.57	133	-	0%	2.57
7-Jan	1430-1650	3	3.34	2.37	134	-	0%	2.37
Average			3.40	3.23	134	-	0%	3.23

Since the Hg SCEM measurements were on the west side of the plant while the stack measurements were conducted on the mixed gas from both sides of the plant, it is possible that the mercury concentrations in the flue gas exiting the east baghouse were lower than those from the west, leading to the observed differences measured by the two methods in different locations. On January 7, since all of the flue gas was scrubbed, oxidized mercury removal across the FGD absorbers would tend to minimize the effects of any side-to-side biases.

Oxidation Catalyst Process Economics

A primary objective of this test program has been to develop the information required to size catalysts for future full-scale installations, and to determine catalyst life. Both of these are components of the cost of oxidation catalyst technology for enhancing mercury capture in plants that have wet FGD systems. Now that testing has been completed at two sites, these data can be used to estimate process costs for scrubbed plants that fire these two coal types and that have similar particulate control device configurations.

Estimated Economics for a North Dakota Lignite/ESP Configuration

Cost estimates have been developed for a single, 500-MW plant in North Dakota that fires North Dakota (ND) lignite. The required mercury control percentage was based on the minimum specified in NETL solicitation DE-PS26-03NT41718 (Large-scale Mercury Control Technology Field Testing Program – Phase II), 55% for lignite fuels. This percentage represents a mercury removal increase beyond the “baseline” removal for the plant being considered.

Preliminary economics for the mercury oxidation catalyst process were developed several years ago as part of a previous NETL Cooperative Agreement, DE-AC22-95PC95260, which involved shorter-term tests and small, sand-bed catalytic reactors.[2] Those economics were based on an assumed catalyst life (3 years) and an assumption that 80% to 90% mercury capture would be required. Since EPA mercury control level requirements were announced in March 2005, it has become apparent that lignite-fired power plants will not likely have to achieve such a high percentage control of mercury in the lignite. Thus, the current economics differ from the previously developed economics in that actual long-term honeycomb catalyst test data were used to project catalyst life, and a lesser overall mercury control percentage requirement of 55% above the baseline removal was assumed (61% overall mercury capture).

However, an objective included in the Statement of Work for this Cooperative Agreement was to achieve at least 90% oxidation of elemental mercury in the flue gas, and ultimately to achieve at least 90% overall mercury capture, by a unit with a particulate control device followed by a wet scrubber. The economics of achieving this higher-performance objective were also estimated as a sensitivity case.

Assumptions

The candidate plant was assumed to be configured like CCS, with a large, cold-side ESP for particulate control and a wet FGD system for SO_2 control. The wet FGD system was assumed to treat 100% of the flue gas from the unit. Many FGD systems on plants that fire North Dakota lignite, including at CCS, currently bypass as much as 25% of the flue gas around the FGD system. However, for this evaluation it was assumed that the Clean Air Interstate Rule, the recent upswing in SO_2 credit values, and/or other regulatory or economic drivers will lead most scrubbed plants to upgrade to 100% scrubbing, independent of mercury co-removal drivers. Consequently, costs to upgrade an existing FGD system to scrubbing 100% of the flue gas were not included in this evaluation.

The costs for oxidation catalyst technology were compared to projected costs for injecting Norit Darco Hg® carbon to achieve the same minimum mercury capture level. Several assumptions had to be made regarding the base plant before developing these cost estimates, including:

- The flue gas at the ESP outlet contains a minimum of 15% oxidized mercury, with the balance being elemental mercury, although, like at CCS, the oxidation percentage will be higher most of the time;
- The existing ESP is adequately sized to capture activated carbon to maintain particulate emissions compliance;
- No mercury is currently captured with the fly ash in the ESP;
- The wet FGD system will remove a net amount of 90% of the oxidized mercury in the flue gas entering the FGD;
- Carbon injection for mercury capture will not affect the mercury oxidation percentage at the ESP outlet;

- The plant currently sells all of its fly ash (a sensitivity case considers the situation where the plant landfills its fly ash); and
- Fly ash sales would be lost if activated carbon is injected upstream of the ESP for mercury control.

The assumption of 90% net removal of oxidized mercury in the wet FGD system warrants further discussion. This Cooperative Agreement did not include pilot-scale wet FGD tests to verify the ability to remove catalytically oxidized mercury at high efficiency. However, such testing was included as part of a subsequent Cooperative Agreement (DE-FC26-04NT41992) and short-term pilot wet FGD tests were conducted downstream of the oxidation catalysts at CCS. Although there were some mercury measurement difficulties associated with those tests, successful measurements were made downstream of the palladium catalyst in a limestone forced oxidation FGD mode. In that test, the observed removal percentage for oxidized mercury across the pilot wet FGD system was 100% as measured by SCEM, and the net removal of oxidized mercury, after accounting for mercury re-emissions (oxidized mercury that is absorbed into the FGD liquor then reduced back to elemental mercury), was 93%.[10] Thus, 90% net capture of oxidized mercury seems to be a reasonably conservative estimate of FGD mercury capture on which to base these economics.

Table 4-52 summarizes a number of other details that went into the economic analysis.

Table 4-52
Factors Used to Develop ND Lignite Mercury Control Process Economics

Parameter	Value
Palladium catalyst cost, $/ft^3	$1050
Carbon #6 catalyst cost, $/ft^3	$710 to $880
Catalyst disposal cost, $/ton	$200
Activated carbon cost, $/lb f.o.b. Marshall, Texas	$0.45
Activated carbon delivery cost, $/ton-mi.	$0.15 (1300 miles total)
New plant equipment economic life, yrs	15
New plant equipment capital recovery factor	0.12
Fly ash sales price, $/ton	$4.40*
Landfill disposal cost, $/ton	$3.65**
Process utilities cost	Not estimated
Process operating and maintenance labor	Not estimated

*****Value developed from data reported on 2001 EIA-767 form for CCS
******Value reported by CCS plant management

The estimated quantities of catalyst and activated carbon required to achieve an additional 55% mercury removal (or greater) require some discussion. For the catalysts, the minimum 55% additional mercury capture requirement and the assumption of a minimum of 15% oxidized mercury in the ESP outlet flue gas corresponds with a minimum oxidation percentage across the catalyst of 62%. The resulting overall mercury capture would be 61%.

Since the catalysts were observed to degrade in mercury oxidation activity with time in service, it is likely that sufficient catalyst volume would be installed to exceed this minimum by a substantial margin initially, then gradually degrade to that minimum value. At that point, the catalyst would have to be regenerated or replaced.

The activity versus time data for the palladium and C #6 catalysts presented earlier in this section were used to develop linear expressions of catalyst oxidation percentage versus time in service. Assuming the catalysts are installed at the same area/space velocity values as in the pilot unit, these linear equations can be used to predict how long each catalyst can be in service while achieving at least 62% elemental mercury oxidation. For both catalysts, the prediction was 720 to 730 days, or approximately two years.

It was decided to treat two years as the effective life of each catalyst type. After two years the catalyst would either have to be replaced or regenerated. Most plants operate no more than two years without taking at least a one- to two-week outage, which should be an adequate amount of time to change out catalysts.

For activated carbon, it was assumed that enough carbon would have to be injected such that the sum of the mercury removed by carbon injection and subsequently across the FGD system would equal that of the oxidation catalyst process, or 61%. For the FGD capture assumptions stated above, this equated to 55% mercury capture in the ESP. Based on previous full-scale test results on GRE's Stanton Station Unit 1, which fires a similar lignite, an injection rate of about 4 to 6 lb/mmacf of flue gas was estimated to be required with a conventional (not chemically treated) carbon to achieve this control level.[11] A mid-point value of 5 lb/mmacf of flue gas was used for these estimates.

Note that this does not result in a completely comparable situation for mercury capture for the two technologies. For the oxidation catalysts, the overall mercury capture would start at about 85% with fresh catalyst, and gradually degrade to 61% after two years, based on 15% mercury oxidation in the ESP outlet flue gas. In comparison, the activated carbon injection case would achieve a consistent 61% capture over this same period, or a significantly lower percentage than the oxidation catalyst cases, on average. The mercury capture efficiencies for both technologies would increase when the ESP outlet mercury is more highly oxidized than 15%, though.

In a "cap and trade" mercury control scenario, the additional mercury capture with the oxidation catalyst technology (a two-year average of greater than 73% versus 61% with activated carbon) would bring economic benefits to the utility, either by offsetting mercury emissions from other units or potentially through free market emissions credit trading. It might be more equitable to compare the two technologies at their average projected mercury capture percentages rather than at the minimum at the end of the catalyst life cycle for the oxidation catalyst technology. Another

approach is to assume a future mercury credit value, which would be applied to the additional mercury captured by the oxidation catalyst case. A value of $30,000 per pound of mercury removed was assumed as a basis for determining how significantly this additional removal might affect the economics.

Base Case Economics for ND Lignite

Table 4-53 compares the projected economics for carbon injection technology to those for the two more active oxidation catalysts at CCS, palladium and C #6. The cases in the table assume that either catalyst would be replaced after two years, with no attempt at regeneration. The annual cost of each process is shown as a "first-year" cost, meaning the operating and maintenance (O&M) costs and catalyst purchase costs are shown in present day dollars and not "levelized" over the economic life of the control system. Also shown in the table is a first-year mercury removal cost in terms of dollars per pound of mercury removed. This value was calculated assuming a lignite heat content of 6500 Btu/lb, and a mercury concentration of 0.1 ppm.

Table 4-53
Comparison of Base Case Economics for ND Lignite Mercury Control Technologies

Parameter	FGD Carbon Injection	Palladium-based Oxidation Catalyst	C #6 Oxidation Catalyst
Capital Equipment, $1000	$2,115	$1,289	$1,289
Catalyst Cost, $1000	-	$5,518*	$5,371**
Delivered Carbon Cost, $1000/yr	$2,849	-	-
Lost Fly Ash Sales, $1000/yr	$1,121	-	-
Increased Landfill Disposal Costs, $1000/yr	$939	-	-
Subtotal O&M Costs, $1000/yr	$4,909	-	-
Capital Equipment Amortization, $1000/yr	$254	$155	$155
Catalyst Amortization Costs, $1000/yr	-	$3,095	$3,012
Total First-year Costs, $1000/yr	$5,163	$3,249	$3,167
First-year Cost, % of Activated Carbon Cost	-	63	61
Mercury Control Cost, $/lb additional Hg removed	$17,900	$11,300	$11,000

*****Includes delivery, installation, and disposal costs
******Includes delivery, installation, and disposal costs; value shown is based on the lower end of the $710/ft^3 to $860/ft^3 projected catalyst cost

The oxidation catalyst cases assume that either catalyst would be disposed of as a hazardous waste. However, it remains to be determined whether the spent catalysts would be classified as a hazardous waste when tested by the toxicity characteristic leaching procedure (TCLP) to determine the concentrations of hazardous metals in the leachate from the tests.

Also, in the case of the palladium catalyst, there is a market for palladium recovery from spent automotive catalysts, so it is possible that spent mercury oxidation catalysts could also be recycled to recover the palladium content. (The spent catalysts would contain between $500,000 and $1 million worth of palladium at current prices).

The comparisons in Table 4-53 show that even when considering replacing the catalysts every two years, the oxidation catalyst technology can be nearly 40% less costly than activated carbon injection based on the assumptions described above.

It is interesting to note that, although the experimental carbon used to make the C #6 catalyst is three orders of magnitude less costly than palladium on a mass basis, this lower cost does not significantly lower the estimated cost of the C #6 catalyst technology. In fact, the C #6 catalyst costs would be greater than the cost of palladium-based catalyst if the high end rather than the low end of the cost estimate range for the carbon catalyst were used for this comparison ($860/ft^3 vs. $710/ft^3).

There appears to be several reasons why the C #6 catalyst is nearly as expensive as the palladium catalyst. One is that, based on the CCS results, it is estimated to take a greater quantity of the C #6 catalyst to equal the performance of palladium. Another is that the estimated production costs for the experimental carbon catalyst negate much of the expected benefit of the lower raw catalyst material cost, when expressed in dollars per cubic foot of catalyst produced. The raw carbon cost represents less than 10% of the projected cost of the completed catalyst. Finally, the palladium catalyst represents a “commodity,” being produced commercially by a number of competitive suppliers using existing production equipment. The C #6 catalyst production involves proprietary technology, and would be produced by a single supplier using new, dedicated production facilities. These results show that, unless there is a technology breakthrough which lowers the cost of producing the C #6 catalyst, it does not represent a significant potential as a lower cost catalyst compared to palladium.

Sensitivity Case Economics for ND Lignite at 55% Mercury Removal

Much of the cost benefit seen for the two oxidation catalyst technologies in Table 4-53 is derived from the assumption that there are significant fly ash revenues that would be lost if activated carbon injection were to be employed for mercury control. Therefore, a sensitivity case was run for the other extreme, where all of the fly ash is currently disposed of in a landfill, perhaps blended with the FGD byproduct for co-disposal. The results of this sensitivity case are summarized in Table 4-54. The results in the table show that the first-year costs for the oxidation catalyst technologies would be nearly equal to that of activated carbon injection if the catalysts are replaced every two years and the plant does not sell any of its fly ash.

Table 4-54
Comparison of Sensitivity Case Economics for ND Lignite Mercury Control Technologies – No Fly Ash Sales

Parameter	FGD Carbon Injection	Palladium-based Oxidation Catalyst	C #6 Oxidation Catalyst
Capital Equipment, $1000	$2,115	$1,289	$1,289
Catalyst Cost, $1000	-	$5,518*	$5,371**
Delivered Carbon Cost, $1000/yr	$2,849	-	-
Lost Fly Ash Sales, $1000/yr	-	-	-
Increased Landfill Disposal Costs, $1000/yr	$9	-	-
Subtotal O&M Costs, $1000/yr	$2,858	-	-
Capital Equipment Amortization, $1000/yr	$254	$155	$155
Catalyst Amortization Costs, $1000/yr	-	$3,095	$3,012
Total First-year Costs, $1000/yr	$3,112	$3,249	$3,167
First-year Cost, % of Activated Carbon Cost	-	104	102
Mercury Control Cost, $/lb additional Hg removed	$10,800	$11,300	$11,000

*Includes delivery, installation, and disposal costs
**Includes delivery, installation, and disposal costs; value shown is based on the lower end of the $710/ft^3 to $860/ft^3 projected catalyst cost

Results presented earlier in this section showed that the palladium-based catalyst could be regenerated by exposure to heated air. Within the limitations of the test conducted, the C #6 catalyst did not regenerate, though. Therefore, another sensitivity case was run, only for the palladium catalyst, illustrating the effects of catalyst regeneration on oxidation catalyst economics. Sensitivity cases were run both with and without fly ash sales being considered.

Little is known about what minimum conditions (temperature and exposure time) are needed to regenerate the palladium catalyst, how long regenerated catalyst will remain active relative to the activity of fresh catalyst, and how many times a catalyst can be regenerated before it must be replaced. Consequently, it was not feasible to develop a detailed estimate for catalyst regeneration economics. Instead, two simplifying assumptions were made. One was that the catalyst could be regenerated once, after two years in service, then would be discarded after a total of four years of service. The other was that the costs associated with regeneration could be represented as an annual cost, expressed as a percentage of the original catalyst cost. For these sensitivity cases, factors of 5% and 10% were used.

For the palladium catalysts, these regeneration cost factors result in annual charges of $276,000 and $552,000, respectively. These dollar amounts are seen as being relatively conservative, considering they are levied as an annual expense in these economics, while only one regeneration would occur in four years. Also, to put these dollar amounts into perspective, the labor associated with removing and reloading the catalyst modules to effect this regeneration is estimated at less than $200,000, while the fuel cost required to heat the regeneration air was estimated at less than $20,000 per regeneration.

Table 4-55 presents the results of the regeneration cases for the palladium-based catalyst. Cases with and without fly ash sales are shown, at both factor levels for regeneration costs. The results in Table 4-55 show that regeneration would markedly improve oxidation catalyst technology economics. In the case where the plant sells its fly ash, the first-year cost for the oxidation catalyst technology with regeneration ranges from 54% to 59% less than of the activated carbon estimate. Where the plant is not selling its fly ash, regeneration improves the process economics to the point where oxidation catalyst technology is 24 to 33% less costly than conventiontal (not chemically treated) activated carbon injection.

Table 4-55
Comparison of Sensitivity Case Economics for ND Lignite Mercury Control Technologies – Palladium Catalyst with Regeneration

Parameter	With Fly Ash Sales		Without Fly Ash Sales	
	Lower Regeneration Cost Factor*	Higher Regeneneration Cost Factor*	Lower Regeneration Cost Factor*	Higher Regeneration Cost Factor*
Capital Equipment, $1000	$1,289	$1,289	$1,289	$1,289
Catalyst Cost, $1000	$5,518**	$5,518**	$5,518**	$5,518**
Regeneration Cost, annual factor, $1000	$276	$552	$276	$552
Capital Equipment Amortization, $1000	$155	$155	$155	$155
Catalyst Amortization Costs, $1000	$1,666	$1,666	$1,666	$1,666
Total First-year Costs, $1000	$2,096	$2,372	$2,096	$2,372
Corresponding Activated Carbon First-year Costs, $1000	$5,163	$5,163	$3,112	$3,112
First-year Cost, % of Activated Carbon Cost	41	46	67	76
Mercury Control Cost, $/lb additional Hg removed	$7,300	$8,200	$7,300	$8,200

*Lower regeneration cost factor is 5% of initial catalyst cost, higher factor is 10%
**Includes delivery, installation, and disposal costs

These results underscore the importance of regeneration to the process economics. In future process development efforts, more emphasis will be placed on determining minimum requirements for regenerating the palladium and other catalysts, and on determining the active life of regenerated catalysts.

A final sensitivity case considers the potential credit value of additional mercury captured with the catalytic oxidation technology compared to that with conventional activated carbon over the two-year assumed catalyst life (or two-year period between regeneration). As described earlier in this section, based on the assumptions made for calculating these preliminary economics, the average overall mercury capture for the oxidation catalyst case over the two-year period would be over 73%, while the average for the activated carbon injection case would be 61%. For the example 500-MW plant, this higher average would result in 62 lb more mercury being removed annually than for the activated carbon case. At a potential mercury allowance value of $30,000/lb, this additional removal could have a value of $1.86 million annually. Even at a lower assumed allowance value of $10,000/lb, the extra mercury removal could result in $620,000 annually.

Although a comparison table was not prepared showing the effects of the additional mercury capture on mercury control economics, the potential value of this additional mercury capture by the oxidation catalyst technology case represents 20% to 60% of the first year activated carbon cost for the case without fly ash sales. Thus, even for the case where the plant is assumed to not sell its fly ash, where the estimated costs for conventional activated carbon technology were about equal to the oxidation catalyst technology estimates (see Table 3-30), the value of the additional mercury captured with the oxidation catalyst technology could represent a substantial cost advantage of 20 to 60%.

Sensitivity Case Economics for ND Lignite at 90% Mercury Oxidation

As mentioned above, an objective included in the Statement of Work for this Cooperative Agreement was to achieve at least 90% oxidation of elemental mercury in the flue gas, and ultimately to achieve at least 90% overall mercury capture on a unit with a particulate control device followed by a wet scrubber. The economics of achieving this higher-performance objective were also estimated as a sensitivity case.

At CCS, the first half of this objective, of achieving at least 90% oxidation of elemental mercury in the flue gas, could readily be achieved with the oxidation catalysts. However, the second half of the objective, of 90% overall mercury capture from the flue gas, proves to be more difficult to realize. The proposal to NETL to conduct this project at CCS was originally prepared during calendar year 2000. Since then, the knowledge base has advanced considerably regarding the capture of mercury by wet FGD systems. In 2000 it was not anticipated that mercury re-emissions would limit oxidized mercury capture in a limestone forced oxidation wet FGD system. This phenomenon was observed during the testing at CCS, and has implications on the ability to achieve the mercury capture criterion listed above.

In the assumptions listed earlier, the wet FGD system achieves only 90% net removal of oxidized mercury. Therefore, it would take essentially 100% mercury oxidation across the catalyst to

achieve 90% overall mercury capture. This is not a realistic target if the net oxidized mercury removal across a full-scale wet FGD system is limited to 90%, but could be realized if higher net removal (near 100%) can be achieved.

Consequently, this higher-performance sensitivity case was evaluated at a condition where the first half of the objective, of achieving at least 90% mercury oxidation at the catalyst outlet, is achieved for the minimum baseline mercury oxidation percentage downstream of the ESP used in this economic evaluation, 15%. Approximately 88% elemental mercury oxidation across a catalyst would be required to achieve 90% overall mercury oxidation. Assuming the 90% oxidation objective is required on an annual average basis, a fresh catalyst would begin the year above this target level, then deactivate to below this level as the year progresses. The corresponding average mercury capture by the FGD system would be 81%, rather than the 90% stated in the objective above.

To average 88% oxidation across the catalyst, the catalyst would have to be replaced or regenerated when the deactivated performance dropped to approximately 81% oxidation across the catalyst. For the palladium catalyst, the CCS data were used to estimate that this oxidation percentage would occur after 300 days of operation on a fresh catalyst. To allow the performance objective to be achieved on an annual (rather than 300-day) basis, the amount of catalyst installed was increased by 15% compared to the previous cases, which should lengthen the period over which 90% total mercury oxidation is achieved as an average to a full year.

It was assumed that to be cost effective, the catalyst would have to be regenerated rather than replaced every year, so the C #6 catalyst was not evaluated for this sensitivity case. The regeneration case was calculated at the higher, 10% catalyst regeneration cost factor used in the cases described above, to account for the more frequent regeneration requirement, but a four-year catalyst life was still assumed. Also, a case was calculated for the palladium catalyst as a “throw away” process.

The results of these estimates are shown in Table 4-56. Note that the table does not include any comparison economics for activated carbon injection, as the available data suggest that conventional (not chemically treated) activated carbon injection cannot achieve 81% mercury capture (78% capture across the ESP) for a plant that fires ND lignite and has an ESP for particulate control.[11]

The results in the table show that if regeneration can be employed annually to maintain an average of 90% mercury oxidation at the FGD inlet, and to extend the catalyst life to four years, the annual cost per pound of additional mercury removed is relatively attractive, at $6,600/lb. For the case where the catalyst is replaced annually, the annual costs are estimated to more than double compared to the case where the catalyst is regenerated. However, in spite of this increase, the calculated cost per pound of mercury removed is competitive with the estimate shown previously in Table 4-53 for conventional activated carbon injection to achieve 55% mercury capture across the ESP.

Table 4-56
High Removal Sensitivity Case Economics for ND Lignite Mercury Control – Palladium Catalyst with and without Regeneration

Parameter	Palladium-based Oxidation Catalyst – with Annual Regeneration	Palladium-based Oxidation Catalyst – with Annual Catalyst Replacement
Capital Equipment, $1000	$1,289	$1,289
Catalyst Cost, $1000	$6,346*	$6,346*
Regeneration Cost, annual factor, $1000	$635	$0
Capital Equipment Amortization, $1000/yr	$155	$155
Catalyst Amortization Costs, $1000/yr	$1,916	$6,346
Total First-year Costs, $1000/yr	$2,705	$6,501
First-year Cost, % of Activated Carbon Cost	Not Applicable	Not Applicable
Mercury Control Cost, $/lb additional Hg removed	$6,600	$15,900

*Includes delivery, installation, and disposal costs

Estimated Economics for a PRB-fired Plant with a Baghouse

A second set of cost estimates was developed for a single, 500-MW plant in Texas that fires PRB coal, and that has a reverse-gas baghouse for particulate control and a wet FGD system for SO_2 control. Two levels of required additional mercury control were considered. The first was the objective stated in the Cooperative Agreement Statement of Work, of achieving at least 90% oxidation of elemental mercury in the flue gas, and ultimately achieving at least 90% overall mercury capture.

Since EPA mercury control level requirements were announced in March 2005, it has become apparent that most subituminous-coal-fired power plants will not likely have to achieve such a high percentage control of mercury in the flue gas. Thus, for the second case a seemingly lesser mercury control percentage requirement was assumed based on the minimum specified in NETL solicitation DE-PS26-03NT41718 (Large-scale Mercury Control Technology Field Testing Program – Phase II), 65% for subituminous coals. This 65% value is interpreted as an improvement in mercury removal beyond the removal achieved by the candidate plant prior to the retrofit of mercury controls.

Assumptions

The plant was assumed to be configured like Spruce, with a large, reverse-gas baghouse for particulate control followed by a wet FGD system for SO_2 control. The wet FGD system was assumed to treat 100% of the flue gas from the unit. Many FGD systems on plants that fire PRB,

including at Spruce, currently bypass as much as 25% of the flue gas around the FGD system. However, for this evaluation it was assumed that factors such as the Clean Air Interstate Rule, the recent upswing in SO_2 credit values, installation of new coal-fired capacity, and/or other regulatory or economic drivers will lead most scrubbed plants to upgrade to 100% scrubbing, independent of mercury co-removal issues. Consequently, costs to upgrade an existing FGD system to scrubbing 100% of the flue gas were not included in this evaluation.

The costs for oxidation catalyst technology were compared to projected costs for injecting Norit Darco Hg® carbon to achieve the same mercury capture levels. Several additional assumptions had to be made regarding the base plant before developing these cost estimates, including:

- The flue gas at the baghouse outlet contains a minimum of 60% oxidized mercury (the observed minimum daily average at Spruce) and an average of 81% oxidized mercury (the average of 22 separate daily average measurements made by SCEM at Spruce over the course of the long-term catalyst test), with the balance being elemental mercury;
- Five percent of the coal mercury is currently captured with the fly ash in the baghouse (nominally the percentage capture measured across the baghouse in January 2004);
- The wet FGD system will remove a net amount of 90% of the oxidized mercury in the flue gas entering the FGD;
- Carbon injection for mercury capture will not affect the mercury oxidation percentage at the baghouse outlet (there are not sufficient field data available to determine whether or not this assumption will hold true; if carbon injection increases the oxidation of the mercury in the flue gas going to the wet FGD system, it will reduce the amount of carbon required to achieve a given overall mercury removal percentage);
- The plant currently sells all of their fly ash (a sensitivity case considered the situation where the plant landfills their fly ash); and
- Fly ash sales would be lost if activated carbon is injected upstream of the baghouse for mercury control.

The assumption of 90% net removal of oxidized mercury in the wet FGD system warrants further discussion. This Cooperative Agreement did not include pilot-scale wet FGD tests to verify the ability to remove catalytically oxidized mercury at high efficiency. However, such testing was included as part of a subsequent Cooperative Agreement (DE-FC26-04NT41992) and short-term pilot wet FGD tests were conducted downstream of the oxidation catalysts at Spruce Plant. In those tests, the observed removal percentage for oxidized mercury across the pilot wet FGD system averaged 93% for tests conducted downstream of all four catalysts, as measured by the Ontario Hydro method.[12]

However, the average net removal of oxidized mercury was considerably lower after the effects of mercury re-emissions (reduction of oxidized mercury in the FGD liquor back to the insoluble elemental form) were considered. The average net removal was calculated as the FGD inlet oxidized mercury concentration minus the FGD outlet oxidized mercury concentration and the observed increase in elemental mercury concentration across the wet FGD system (presumed to be due to re-emissions), all divided by the inlet oxidized mercury concentration.

At Spruce, the net oxidized mercury removal across the wet FGD pilot (after considering re-emission effects) averaged 80%, ranging from 71% for the test downstream of the Pd catalyst to 96% for the test downstream of the C#6 catalyst. The average for the gold catalyst was 81%.[12]

It should be noted that these tests were conducted in a limestone, forced oxidation mode, whereas the existing FGD system at Spruce currently operates in a limestone, natural oxidation mode that produces gypsum as a byproduct. CPS Energy advised URS that in the future, if they convert the FGD system at Spruce to scrubbing 100% of the flue gas, they also plan to convert to forced oxidation to ensure that all of the SO_2 removed will be fully oxidized. Thus, these pilot tests were conducted in a forced oxidation mode.

It was somewhat surprising that evidence of mercury re-emissions was seen in the results of these pilot-scale limestone forced oxidation tests. Previous data from the EPA Information Collection Request suggested that mercury re-emission was not a significant issue for wet FGD systems that operate in a limestone forced oxidation mode.[1]

It is believed that the average of 80% net removal of oxidized mercury by the pilot wet FGD system is low, for a couple of reasons. One is that due to the limited height of the portable, pilot wet FGD absorber, its gas-film limit to mass transfer is lower than for a well-designed full-scale absorber. During the pilot-scale testing at Spruce, the pilot wet FGD absorber was typically limited to just over 90% SO_2 removal at conditions where a well-performing, full-scale absorber would achieve over 95% removal. Oxidized mercury is very soluble in FGD liquors, and should be removed from the flue gas at an efficiency near the absorber's gas-film limit. For this reason, it is felt that the observed oxidized mercury capture percentage average of 93% (not considering re-emissions) is lower than could be realized in a full-scale absorber.

Second, two other NETL cooperative agreements are investigating mercury re-emissions from wet FGD systems and methods of limiting or eliminating re-emissions (DE-FC26-04NT42309 and DE-FC26-04NT42314). While these projects are still underway, it is anticipated that through the use of additives such as Degussa Corporation's TMT-15 or by controlling FGD chemistry, mercury re-emissions from wet FGD systems can be cost effectively controlled. As an example, recent testing with this same pilot wet FGD system downstream of a pilot-scale gold oxidation catalyst on a plant that fires PRB showed that TMT-15 could be added to the FGD recycle slurry to achieve 97% capture of oxidized mercury across the absorber with no re-emissions.[13] It would clearly be more cost effective to use an additive to control re-emissions from an FGD system than to use more catalyst to achieve higher mercury oxidation percentages to offset re-emission effects.

It is likely that by controlling re-emissions, and with an absorber with a higher gas-film mass transfer limit, net oxidized mercury capture percentages greater than 95% can be achieved. However, the 90% value used in these cost estimates was seen as a relatively conservative target for optimized FGD mercury capture. Also, the cost estimates include the cost of Degussa's TMT-15 as an FGD additive, at the manufacturer's recommended dosage for controlling re-emissions.

Table 4-57 summarizes a number of other details that went into the economic analyses.

Table 4-57
Factors Used to Develop Mercury Control Process Economics

Parameter	Value
Palladium catalyst cost, $/ft^3	$1,050
Catalyst disposal cost, $/ton	$200
Activated carbon cost, $/lb f.o.b. Marshall, Texas	$0.45
Activated carbon delivery cost, $/ton-mi.	$0.15 (300 miles total)
TMT-15 cost, $/kg delivered to Central Texas	$5.00
New plant equipment economic life, yrs	15
New plant equipment capital recovery factor	0.12
Fly ash sales price, $/ton	$5.00*
Incremental landfill disposal cost, $/ton	$3.00*
Process utilities cost	Not estimated
Process operating and maintenance labor	Not estimated

*****Value developed from data reported on 2001 EIA-767 form for scrubbed plants that fire low-sulfur Western coals

Mercury Control Targets

Some discussion is also required about the ability to meet the two mercury oxidation and removal level requirements described at the beginning of this subsection, considering the data collected at Spruce Plant. The proposal to NETL to conduct this project at Spruce Plant was originally prepared during calendar year 2000. Since then, the state of the art has advanced considerably regarding the effects of fuel type and of existing air pollution control technologies on mercury oxidation and capture. As examples, in 2000 it was not expected that mercury in the flue gas downstream of a reverse-gas baghouse on a plant that fires PRB would be highly oxidized, or that mercury re-emissions could limit oxidized mercury capture in a limestone forced oxidation wet FGD system. Both of these phenomena were observed during the testing at Spruce Plant, and have implications on the ability to achieve the mercury oxidation and capture criteria described earlier in this subsection.

The first performance level considered, as stated in the Cooperative Agreement Statement of Work, was achieving at least 90% oxidation of elemental mercury in the flue gas, and ultimately achieving at least 90% overall mercury capture from the flue gas. At Spruce, the first half of this objective, of achieving at least 90% oxidation of elemental mercury in the flue gas, could readily be achieved with the oxidation catalysts. For the average mercury oxidation observed downstream of the baghouse at Spruce Plant, 81%, only 47% elemental mercury oxidation across a catalyst was required to achieve 90% overall mercury oxidation. For the lowest daily average

mercury oxidation percentage measured downstream of the baghouse during this project, 60%, it would take 75% elemental mercury oxidation across the catalyst to achieve 90% overall mercury oxidation.

However, the second half of that objective, of 90% overall mercury capture from the flue gas, proves to be more difficult to realize. Based on the assumptions listed above, the wet FGD system would achieve only 90% net removal of oxidized mercury. Therefore, it would take essentially 100% mercury oxidation across the catalyst to achieve 90% overall mercury capture. This is not a realistic target if the net oxidized mercury removal across the full-scale wet FGD system is limited to 90%, but could be realized if higher net removal of oxidized mercury can be achieved.

Consequently, the first performance requirement case was evaluated at a condition where the first half of the objective, of achieving at least 90% mercury oxidation at the catalyst outlet, was achieved for the minimum mercury oxidation measured at Spruce (60%). This corresponds with a minimum of 75% oxidation of elemental mercury across the catalyst. But, the corresponding overall mercury capture percentage would be at least 82%, rather than the desired 90%.

For the second performance requirement case, a seemingly lesser mercury control percentage requirement was assumed, 65% mercury removal compared to baseline mercury emissions at the candidate plant. The 65% additional mercury capture would be possible to achieve for the lowest baseline oxidation percentage seen downstream of the baghouse at Spruce (60%), However, it would be virtually impossible to achieve for the average baseline oxidation (81%) downstream of the baghouse. Again, it is the assumption of 90% capture of oxidized mercury across the wet FGD system (rather than a higher percentage) that causes this limitation.

As an example, at the minimum oxidation percentage measured downstream of the catalyst at Spruce Plant, if it is still assumed that the baghouse removes 5% of the coal mercury, the FGD system would remove 90% of the 60% oxidized, of the remainder downstream of the baghouse (95% of the coal mercury). This corresponds with 56.3% baseline mercury capture. A 65% improvement would be to remove 65% of the 43.7% not captured, or an improvement to 84.7% overall mercury capture. It would take 93.2% elemental mercury oxidation at the catalyst outlet, or 83.0% oxidation across the catalyst, to achieve this overall mercury capture level based on 90% capture of oxidized mercury across the wet FGD system.

Making these same estimates for the *average* mercury oxidation percentage at the baghouse outlet (81%), the baseline overall mercury capture would be 74.3%, and removing 65% of the remaining mercury would raise the overall mercury capture requirement to 91.0%. Even if the mercury can be100% oxidized at the catalyst outlet, the maximum mercury capture that could be achieved according to these assumptions would be 90.5% (5% plus 90% of the remaining 95% of the coal mercury). Thus, on average, the goal of 65% capture of the baseline mercury emissions could not be achieved at Spruce Plant according to these assumptions.

After considering this second case, and the inability to achieve the 65% mercury capture target on average, it was decided to first evaluate the economics of for the first performance scenario (a minimum of 90% mercury oxidation at the catalyst outlet, corresponding with 75% minimum

oxidation of elemental mercury across the catalyst and a minimum of 82% overall mercury capture). If the economics of the mercury oxidation catalyst technology appeared to be competitive or advantageous compared to conventional activated carbon injection at these conditions, cases requiring higher mercury oxidation percentages across the catalyst would be considered. However, as described below, the economics were not favorable for the oxidation catalyst technology, so no additional performance levels were evaluated.

Performance Estimates for Oxidation Catalysts and for Conventional Activated Carbon Injection

The estimated quantities of catalyst to achieve a minimum of 90% overall mercury oxidation and the amount of activated carbon required to achieve the corresponding minimum of 82% overall mercury removal require discussion. For the catalysts, 90% mercury oxidation percentage at the catalyst outlet and a minimum of 60% oxidized mercury in the baghouse outlet flue gas corresponds with an oxidation percentage across the catalyst of 75%. Since the catalysts were observed to degrade in mercury oxidation activity with time in service, it is likely that sufficient catalyst volume would be installed to exceed this minimum by a substantial margin initially, then gradually degrade to 75% as a minimum value. At that point, the catalyst would have to be regenerated or replaced.

The activity versus time data presented earlier in this section showed that the Pd and gold catalysts were the most active through the end of the test period, and that both were readily regenerated with hot air. The activity results for these two catalyst types from initial startup in September 2003 through February 2004 showed a considerable amount of scatter. The results from May 2004 through April 2005 were more consistent, and showed a generally linear decrease in activity versus time in service. The May 2004 results were the first measured with a newer SCEM with a more sensitive atomic absorption spectrometer, better suited to the low elemental mercury concentrations seen at the Spruce baghouse outlet.

For this reason, it is thought that the later data better represent the actual activity of these catalysts when expressed as percent elemental mercury oxidation across the catalyst. The May 2004 through April 2005 data were therefore used to develop linear expressions of catalyst oxidation percentage versus time in service. For the time prior to May 2004, it was assumed the oxidation percentages were at least as high as the May 2004 value. Assuming full-scale catalysts would be installed at the same area/space velocity values as in the pilot unit, these linear equations were used to predict how long each catalyst could be in service while achieving at least 75% mercury oxidation. For both catalysts, the prediction was about one year.

It was therefore decided to treat one year as the effective catalyst life. After one year the catalyst would either have to be replaced or regenerated. It was also decided to do the economic estimates for the palladium catalyst, which saw slightly better end-of-test oxidation performance than the gold catalyst. The economics for gold catalyst should be similar.

For activated carbon, it was assumed that enough carbon would have to be injected so the sum of the mercury removed by carbon injection and subsequently across the FGD system would total 82%. For the FGD capture assumptions stated above, this equated to 61% mercury capture across

the baghouse (including the baseline capture of 5%). Based on previous EPRI pilot-scale test results on PRB-fired plants, an injection rate of about 0.6 lb/mmacf of flue gas was estimated to be required with FGD carbon to achieve this control level.[14]

Base Case Economics

Table 4-58 compares the projected economics for carbon injection technology to those for one of the two more active oxidation catalysts at Spruce, palladium. This assumes that the catalyst would be replaced after one year, with no attempt at regeneration (a later sensitivity case considers the effects of regeneration). The annual cost of each process is shown as a "first-year" cost, meaning the operating and maintenance (O&M) costs and catalyst purchase costs are shown in present day dollars and not "levelized" over the economic life of the control system. For both processes, an equivalent mercury control cost is shown in dollars per pound of mercury removed (beyond the baseline removal).

Table 4-58
Comparison of Base Case Economics for Mercury Control Technologies

Parameter	FGD Carbon Injection	Palladium-based Oxidation Catalyst
Capital Equipment, $1000	$1,391	$3,278
Catalyst Cost, $1000	-	$3,336*
Delivered Carbon Cost, $1000/yr	$253	-
TMT-15 FGD Additive Costs, $1000/yr	$249	$249
Lost Fly Ash Sales, $1000/yr	$489	-
Increased Landfill Disposal Costs, $1000/yr	$296	-
Subtotal O&M Costs, $1000/yr	$1,286	$3,585
Capital Equipment Amortization, $1000/yr	$167	$393
Total First-year Cost, $1000/yr	$1,453	$3,978
First-year Cost, % of Activated Carbon Cost	-	270
Mercury Control Cost, $/lb additional Hg removed	$17,600	$48,100

*****Includes delivery, installation, and disposal costs

The oxidation catalyst case assumes the spent catalyst would be disposed of as a hazardous waste. However, it remains to be determined whether the spent catalysts would be classified as a hazardous waste when tested by the toxicity characteristic leaching procedure (TCLP) to determine the concentrations of hazardous metals in the leachate from the tests. Also, there exists a significant market for palladium recovery from spent catalysts, so it is possible that the spent

mercury oxidation catalysts could also be recycled to recover the palladium content. (The spent catalysts would contain over $500,000 worth of palladium at current prices).

The comparison in Table 4-58 shows that when replacing the catalyst every year, the oxidation catalyst technology is over two and a half times the cost of the activated carbon injection technology. There are several reasons why the oxidation catalyst technology fares poorly in this comparison.

One is that activated carbon injection upstream of a reverse-gas baghouse on a plant that fires low-sulfur coal represents a best case for that technology, as the filter bags serve as a fixed bed reactor for the injected carbon. Much higher carbon injection rates would be required for a plant that has an ESP for the particulate control device.

A second reason is that the requirement of a minimum of 75% oxidation across the catalyst bed and the assumption of no regeneration results in a short catalyst life of only one year. A one-year catalyst life was never expected to be cost effective for this technology. A sensitivity case presented below shows the effects of catalyst regeneration on the economics.

A third reason is that the duct configuration with a baghouse rather than an ESP as the particulate control device is less advantageous for retrofitting a catalyst. With an ESP, the catalyst could be retrofit into the ESP outlet nozzle, whereas due to the duct configuration of a reverse-gas baghouse, a separate catalyst chamber would most likely have to be installed in the duct run between the baghouse and FGD system. The capital cost estimate for the oxidation catalyst case reflects the retrofit of two such chambers, assuming the candidate plant would have two separate baghouse modules.

Sensitivity Case Economics

Results presented earlier in this section showed that both the palladium-based and gold-based catalysts could be regenerated by exposure to heated air. Previous economic analyses conducted based on results from CCS showed a significant improvement in the cost effectiveness of oxidation catalyst technology if regeneration can be employed to extend catalyst life. Therefore, a sensitivity case was run for the palladium catalyst illustrating the effects of catalyst regeneration on economics for a plant that fires PRB and that has a baghouse for particulate control.

Little is known about what minimum conditions (e.g., temperature and exposure time) are needed to regenerate the palladium catalyst, how long regenerated catalyst will remain active relative to the activity of fresh catalyst, and how many times a catalyst can be regenerated before it must be replaced. Current testing as part of Cooperative Agreement DE-FC26-04NT41992 is comparing the activity of regenerated catalysts from this project (41185) to the activity of fresh catalysts, although in flue gas conditions corresponding with the new tests sites. Also, EPRI-funded laboratory testing is planned to conduct a parametric evaluation of regeneration conditions on spent catalysts from the 41992 project. However, these results are not yet available to serve as a basis for the current economics. Consequently, it was not feasible to develop a detailed estimate for catalyst regeneration economics. Instead, two simplifying assumptions were

made. One was that the catalyst could be regenerated annually, then would be discarded after a total of four years of service. The other was that the costs associated with regeneration could be represented as an annual cost, expressed as a percentage of the original catalyst cost. For these sensitivity cases, a factor of 10% was used. This regeneration cost factor results in an annual charge of $334,000.

For the economics previously discussed for a palladium catalyst under North Dakota lignite conditions, a lower factor of 5% for regeneration costs was also considered. However, that case required only one regeneration in four years, while the current case would require three regenerations in four years. Thus, only the higher factor of 10% was considered for the PRB/baghouse case.

Table 4-59 presents the results of the regeneration case for the palladium-based catalyst. The results show that regeneration would markedly improve oxidation catalyst technology economics, but the annual cost is still estimated to be about 36% higher than for activated carbon injection.

Table 4-59
Comparison of Sensitivity Case Economics for Mercury Control Technologies – Palladium Catalyst with Regeneration

Parameter	FGD Carbon Injection	Palladium-based Oxidation Catalyst
Capital Equipment, $1000	$1,391	$3,278
Catalyst Cost, $1000	-	$3,336**
Annual Catalyst Regeneration Cost, $1000/yr	-	$334
Delivered Carbon Cost, $1000/yr	$253	-
TMT-15 FGD Additive Costs, $1000/yr	$249	$249
Lost Fly Ash Sales, $1000/yr	$489	-
Increased Landfill Disposal Costs, $1000/yr	$296	-
Subtotal O&M Costs, $1000/yr	$1,286	$583
Capital Equipment Amortization, $1000/yr	$167	$393
Catalyst Cost Amortization, $1000/yr	-	$1,007
Total First-year Costs, $1000/yr	$1,453	$1,983
First-year Cost, % of Activated Carbon Cost	-	136
Mercury Control Cost, $/lb additional Hg removed	$17,600	$24,000

*Regeneration cost factor is 10% of initial catalyst
**Includes delivery, installation, and disposal costs

A portion of the cost benefit for the oxidation catalyst technology in Tables 4-58 and 4-59 is derived from the assumption that there are fly ash revenues that would be lost if activated carbon injection were to be employed for mercury control. The other extreme might be for a plant where all of the fly ash is currently disposed of in a landfill, perhaps blended with the FGD byproduct for co-disposal, so there would be no fly ash sales revenue to lose and little increase in landfill costs.

Because the economic analyses in Tables 4-58 and 4-59 already show the catalytic oxidation technology to be more costly than ACI in the case with ash sales, cases without ash sales would clearly be even less cost effective. These cases were calculated, but the results are not shown in detail here. However, as an example of the results, for the situation where the catalyst is regenerated annually, if there are no existing fly ash sales, the relative cost of the oxidation catalyst technology goes from being 36% higher than for conventional activated carbon injection to almost three times the cost.

These results show that an existing, scrubbed plant that fires PRB and that has a baghouse for particulate control is not likely to be a good candidate for the retrofit of a mercury oxidation catalyst to enhance mercury capture. For the assumptions used to develop these economics, it would be more cost effective to retrofit conventional activated carbon injection, even if it resulted in lost fly ash sales.

The authors expect that the economics of oxidation catalyst versus conventional activated carbon would be much more favorable for a scrubbed plant that fires PRB but that has an ESP for particulate control. In such a configuration, it would be expected that the baseline mercury oxidation at the ESP outlet would be less than 20%, and mercury capture by the ESP and wet FGD system would be at a lower percentage than that. This would greatly improve the cost effectiveness of oxidation catalyst technology when expressed in terms of dollars per pound of mercury removed. Furthermore, it would take substantially more carbon injected upstream of the ESP than upstream of a baghouse to achieve high mercury removal percentages, increasing the effective cost per pound of mercury removed by that technology.

Some thought was given to using the Spruce catalyst results to generate rough economics for a PRB case with an ESP rather than a baghouse for the particulate control device upstream of the catalyst. However, because the data collected at Spruce reflected such high elemental mercury oxidation upstream of the catalyst, it was deemed to introduce too much technical risk to extrapolate these results to a flue gas with much higher elemental mercury percentages at the catalyst inlet. Instead, the project team is currently testing the gold catalyst downstream of an ESP in a plant that fires PRB.[13]

5
CONCLUSIONS

CCS Results

During initial catalyst pilot unit operation at CCS, it became apparent that fly ash was accumulating on the horizontal-gas-flow catalysts, so provisions were needed to help keep catalyst surfaces cleaner. Sonic horns were retrofitted to each catalyst compartment and proved to be effective at preventing fly ash buildup in three of the four catalysts, but less effective for the fourth, SBA #5 catalyst. However, the fourth catalyst material is from a single source, and available in relatively limited quantities. Therefore, it is of little future commercial interest for the oxidation catalyst technology.

Based on this experience, it is apparent that some mechanism will be required for keeping catalysts clean if they are installed in a horizontal-gas-flow configuration downstream of an ESP. Sonic horns may be acceptable, if they can be installed to provide a similar level of sonic energy as was applied in the pilot unit over the entire catalyst cross section. Air soot blowers may also be an applicable technology to prevent fly ash buildup in future full-scale installations. It also may be desirable to employ catalysts with larger cell dimensions, which may be easier to keep clean. Finally, it may be easier to keep a single, 9-in. catalyst layer clean than the three 3-in. layers as the palladium-based and C #6 catalysts were installed in this pilot unit. Alternately, in a full-scale application horns may need to be installed between catalyst layers.

Mercury SCEM results show that after 13 to 21 months of operation at CCS, the Pd #1 and C #6 catalysts remained relatively active for oxidizing the inlet flue gas elemental mercury, while the SCR and SBA #5 catalysts were much less active. Consequently, of the four catalysts tested at CCS, only the Pd #1 and C #6 catalysts appear to be viable for commercial installation on plants that fire North Dakota lignite. As operated at CCS, both initially achieved approximately 95% oxidation of elemental mercury across the catalyst, and both lost activity at a linear rate over time, dropping about 0.05% oxidation per day in service. These linear activity loss rate data were used to extrapolate catalyst performance over greater periods of operating time.

However, it should be noted that the palladium-based and C #6 were operated at different area velocity values. Thirty percent less of the palladium-based catalyst was required than the C #6 catalyst to achieve the performance detailed above.

Gas characterization by the Ontario Hydro method at CCS did not show good agreement with the results from the EPRI Hg SCEM used to routinely measure catalyst activity, particularly for the C #6 and SCR catalysts. For these catalysts, the Ontario Hydro method generally showed greater oxidation percentages across the catalyst (better catalyst performance) than the Hg SCEM. It is not certain which method results are biased. However, there is circumstantial evidence that the

error is with the Ontario Hydro method. In this report, the more conservative (less optimistic) Hg SCEM results have been used as the primary basis for analyzing and reporting catalyst performance.

Additional gas sampling showed very little oxidation of SO_2 to increase sulfuric acid concentrations in the flue gas across the mercury oxidation catalysts, and no oxidation of NO to NO_2. These are both positive results, as significant oxidation of either of these species across the mercury oxidation catalysts could have produced undesirable balance-of-plant effects.

Catalyst thermal regeneration tests conducted at the end of the 21-month test period at CCS showed that two of the three catalysts tested for regeneration, the palladium and SCR catalysts, could have their elemental mercury oxidation performance substantially restored. The third catalyst, C #6, showed no improvement at the relatively mild regeneration conditions (600^{o}F air flowing at about 14% of the normal flue gas flow rate through the catalysts). These results indicate that, at least for the palladium catalyst, thermal regeneration may offer a cost effective approach for extending catalyst life and improving process economics.

The catalyst activity versus time data from CCS were used to develop comparative economics for the oxidation catalyst technology and a more conventional activated carbon injection approach, both for a scrubbed plant that fires North Dakota lignite and that must achieve at least 55% additional mercury capture. These comparative economics showed that for a plant that currently sells its fly ash, oxidation catalyst technology could achieve greater than 55% increased mercury control at a cost 30 to 40% less than by injecting Norit Darco Hg® activated carbon. This assumes the catalyst is used two years then discarded. However, if the plant does not currently sell its fly ash, the activated carbon case was slightly less costly than the catalyst case.

Regeneration can greatly improve the cost effectiveness of the oxidation catalyst technology. Although regeneration costs could not be definitively estimated, sensitivity cases were run using two different estimated regeneration cost values. These cases showed that for a plant that currently sells its fly ash, regenerating the palladium catalyst once to allow it to remain in service for a total of four rather than two years, improved the process economics to where oxidation catalyst technology costs were 50 to 60% lower than activated carbon injection costs. Even in the case where the plant does not sell its fly ash, the regeneration scenario improved the economics of the oxidation catalyst technology to the point where it was estimated to be 20 to 30% lower in cost than activated carbon injection as opposed to nearly equal in cost without regeneration.

These cost estimates allow two conclusions to be drawn from the results at CCS. One is that, based on current cost estimates for producing commercial quantities of the C #6 catalyst, it does not appear to be significantly less costly than the palladium catalyst. This is despite the fact that palladium is over 1000 times the cost of the C #6 raw carbon material on a mass basis. The other conclusion is that regeneration will be very important to the future economics of this developing mercury control technology.

These two conclusions raise question as to whether development resources should continue to be invested in the experimental, C #6 catalyst, or whether more emphasis should be placed on developing regeneration technology for the palladium-based catalysts (and/or gold as was tested

at Spruce plant). However, given the site specificity seen in catalyst performance in previous, smaller-scale catalyst tests, it remains worthwhile to continue to test as wide a range of catalyst types as possible at pilot scale.

Spruce Results

Operation of oxidation catalysts downstream of a reverse-gas baghouse proved to be advantageous from the standpoint of fly ash buildup in the horizontal-gas-flow catalysts cells. At CCS, downstream of a high-efficiency ESP, sonic horns were required to prevent fly ash buildup in the catalysts. However, at Spruce Plant, sonic horns were not needed. Catalyst pressure drop remained low (below 1 in. H_2O [0.25 kPa]) and fly ash buildup within the catalyst cells was minimal over nearly 18 months of operation.

The reverse-gas baghouse upstream of the oxidation catalyst pilot unit had what was at the time an unexpected effect on mercury oxidation, though. It was expected that the flue gas at this PRB-fired unit would contain mostly elemental mercury and less than 20% oxidized mercury. This was the case upstream of the baghouse, where only 5 to 16% mercury oxidation was measured, but downstream of the baghouse the mercury in the flue gas averaged 81% oxidation. Since the beginning of this project, it has become more apparent that reverse-gas baghouses on plants that fire PRB can oxidize a significant percentage of the flue gas mercury content.

This high oxidation percentage, along with apparent mercury capture across the baghouse, led to low elemental mercury concentrations at the oxidation catalyst pilot unit inlet – often below 2 $\mu g/Nm^3$ and sometimes below 1 $\mu g/Nm^3$. Furthermore, the total and elemental mercury concentrations were observed to vary over the course of a day, apparently affected by baghouse cleaning cycles. These low, and often variable elemental mercury concentrations made the measurement of catalyst oxidation performance difficult.

A switch to newer SCEMs with more sensitive atomic absorption spectrometers midway through the test period, and, when possible, the use of two SCEMs to simultaneously measure catalyst inlet and outlet mercury concentrations, appeared to improve data quality. These data, from the latter half of the test period, showed the palladium and gold catalysts to be the most active, with the palladium catalyst showing slightly better mercury oxidation performance than the gold at the end of the test. The end-of-test performance for the palladium catalyst, showing 51% oxidation of elemental mercury across the catalyst after nearly 18 months of service, represented more rapid activity loss for this catalyst than was measured at CCS.

For most of this period, the C #6 catalyst showed similar mercury oxidation performance to that of the palladium and gold. However, the end-of-test measurements for that catalyst showed a precipitous drop in oxidation activity. This result, along with the observation that the CCS economics showed no significant cost advantage for the C #6 catalyst compared to palladium, suggests that the experimental carbon-based catalyst will be of lesser interest for future testing of this technology.

The fourth catalyst, the SCR catalyst, showed lower performance than either the palladium or gold catalyst throughout this period. This observation, along with the fact that nearly five times

the catalyst volume was used for the SCR catalyst compared to the palladium or gold catalyst, makes it clear that an SCR-type catalyst will be less cost effective in this low-temperature mercury oxidation application.

As at CCS, the catalysts did not appear to oxidize any of the flue gas SO_2 to SO_3/sulfuric acid. Concentrations of SO_3/sulfuric acid at both the catalyst pilot unit inlet and at the outlets of each catalyst were below 0.1 ppmv, which is generally regarded as a lower detection limit of the Controlled Condensation method used in these measurements.

All of the catalysts were readily regenerated when exposed to heated air overnight. The palladium catalyst recovered from 51% elemental mercury oxidation across the catalyst prior to regeneration to 84% after. The gold catalyst saw a similar improvement, from 47% to 78%. The temperature to which the catalysts themselves were heated was not directly measured, but the hot air exiting the catalyst chamber was heated to approximately 350 to 360^{o}F (177-182^{o}C). This was about 50^{o}F (28^{o}C) cooler than the corresponding temperatures in the regeneration tests conducted at CCS.

It appears that these catalysts lose activity due to adsorption of other flue gas species onto catalyst surfaces, blocking sites where mercury can be adsorbed, oxidized, then desorbed. Results from previous investigations suggest that these competing species may include selenium and sulfur species.[2] Further work is needed to determine the optimum conditions for regenerating the catalysts. It appears that regeneration time, regeneration gas temperature, and regeneration gas flow rate are variables that can be optimized. Also, it needs to be determined whether the regeneration gas can be heated flue gas, or whether a more inert gas such as air is required.

Estimates were made of process economics for a power plant unit that fires PRB, has a reverse-gas baghouse followed by a wet FGD system, and sells all of its fly ash. Costs were estimated for a catalytic oxidation system installed between the baghouse and wet FGD system, and comparison costs were estimated for conventional activated carbon injection. The costs were based on a system designed to achieve at least 75% oxidation of the mercury in the baghouse outlet flue gas. Based on measurements at Spruce Plant over nearly 18 months of pilot unit operation, this catalytic oxidation percentage would ensure that the mercury in the flue gas entering the wet FGD system is always at least 90% oxidized. Assuming the wet FGD system can achieve a net of 90% capture of oxidized mercury, this level of oxidation would ensure at least 82% capture of the coal mercury in the baghouse and wet FGD system.

These estimates showed that under the scenario evaluated, catalytic oxidation technology would not be cost competitive with conventional activated carbon injection. Several effects appear to contribute to this finding. One is that application of activated carbon injection technology is particularly advantageous upstream of a reverse-gas baghouse, as the filter bags tend to serve as fixed-bed reactors and low activated carbon injection rates can achieve high mercury capture percentages. Higher carbon injection rates and/or lower overall mercury capture is typically seen when injecting upstream of an ESP, particularly for plants that fire PRB coal.

Another effect is that with the relatively high mercury oxidation percentage seen at the baghouse outlet at Spruce, it also requires a relatively high mercury oxidation percentage across a

downstream catalyst to significantly improve the overall mercury capture percentage. This high mercury oxidation percentage (75% minimum oxidation across the catalyst) led to an assumption that the catalysts would need to be regenerated or replaced on an annual basis, which is disadvantageous for the oxidation catalyst technology.

A third effect is that due to the configuration of a reverse-gas baghouse, there would not be a convenient location to install oxidation catalysts within the existing equipment. Instead, it was assumed that new catalytic reactors would have to be installed between the baghouse outlets and the wet FGD system. This increased the capital cost requirements of the oxidation catalyst technology.

It was decided that there would be too much technical risk involved in using catalyst performance data from downstream of the baghouse at Spruce to project performance and cost information for a plant that fires PRB and has an ESP for particulate control. However, it is quite apparent from these cost estimates that catalytic oxidation technology would be much better suited to a plant that has an ESP rather than a baghouse. An important testing need for the catalytic oxidation technology is to conduct long-term catalyst tests at a plant that fires PRB and that has an ESP for particulate control. Such testing is currently underway at another site.

Summary of Lessons Learned from the Project

Catalyst Activity

Results are now available from two sites, with four different catalyst types having been evaluated at each site. At both sites, the Pd #1 catalyst was among the top two performing catalysts. At CCS, the C #6 catalyst, as installed with greater catalyst volume, was essentially equal in performance to Pd #1, while at Spruce the gold catalyst was nearly equal in performance.

It is not clear why the C #6 catalyst was not as active at Spruce. Actually, up until October 2004, the C #6 catalyst showed similar performance to both the Pd #1 and gold catalysts. No reason is apparent why the C #6 catalyst experienced such a dramatic loss of activity by February 2005. At both sites, the SCR catalyst was less active than the Pd #1, gold, or C #6.

Conducting the economic analyses described in this report proved to be a very useful exercise in terms of evaluating candidate mercury oxidation catalysts. Both the C #6 and SCR catalysts were evaluated in these pilot units because they were perceived as offering a lower cost alternative to precious metal catalysts such as palladium or gold. However, in conducting the economic analyses it was determined that even for palladium or gold, the active ingredient represents only 10 to 20% of the delivered catalyst cost. The other 80 to 90% of the cost consists of substrates, labor for catalyst processing, purchase of catalyst “cans” or enclosures, labor to load the cans, etc. These costs are more proportional to the volume of catalyst required than what the active ingredient might be.

At both CCS and Spruce, the C #6 catalyst was installed with 44% more catalyst volume than the Pd #1 (or gold at Spruce). This helps explain why, in the economics for a North Dakota lignite

application based on the CCS results, there was little difference in cost between the precious-metal palladium catalyst and the “low cost” experimental carbon catalyst.

The SCR catalyst was installed with over three times the volume of the Pd #1 catalyst at CCS, and nearly five times the volume of the Pd #1 and gold at Spruce. Although costs were not solicited for the SCR catalysts for these economic analyses, it is apparent that even if the SCR catalyst had equaled the performance of the Pd #1 or gold, it would not be economical if it had to be installed at three to five times the catalyst volume.

This understanding of catalyst pricing has helped focus future efforts for developing the mercury oxidation catalyst activity on the Pd #1 and gold catalysts, which require the least catalyst volume to achieve desired oxidation percentages.

The understanding of the oxidation catalyst technology remains somewhat empirical at this point. It is believed that the catalysts lose activity because of adsorption of competing species on active catalyst sites. Testing as part of a previous cooperative agreement suggests that metals such as selenium and other species such as SO_3/sulfuric acid contribute to activity losses.[2] Until these mechanisms are better understood, it will be difficult to predict which flue gases are best suited for this technology or which catalyst might be best for a particular flue gas, and difficult to predict optimum catalyst regeneration conditions.

Flue Gas Mercury Measurements

At the beginning of this project, it was expected that a single Hg SCEM could be cycled from sample point to sample point to evaluate the performance of four catalysts operating in parallel at a given site. As the project progressed, it became apparent that at some plants, hour-to-hour variations in total mercury concentration and mercury oxidation in the flue gas make such measurements more difficult. Furthermore, measurements at Spruce plant indicated that the mercury adsorption capacity of the catalysts was affected by temporal variations in total mercury concentration in the flue gas. As the catalyst inlet total mercury concentration increased, the catalysts adsorbed more mercury, and as the inlet total mercury concentration decreased they could desorb mercury back into the flue gas.

It became apparent as the project progressed that a better measurement scenario was to use two Hg SCEMs, to simultaneously measure the inlet and outlet of a single catalyst for the mercury species of interest (elemental or total mercury).

At Spruce plant, because of the mercury oxidation and removal experienced across the reverse-gas baghouse, it required the measurement of very low elemental mercury concentrations to be able to measure catalyst performance, often in the range of 0.1 to 0.2 $\mu g/Nm^3$. The Hg SCEMs used early in the project were not capable of measuring reliably in this range. However, the economic analysis conducted at the end of this project showed that a site with a reverse-gas baghouse such as Spruce would not be a likely candidate for low-temperature mercury oxidation catalyst technology. CCS was clearly a better candidate for the technology, and the catalyst inlet elemental mercury concentrations of typically greater than 10 $\mu g/Nm^3$ posed no problems for

measuring catalyst performance. Catalyst outlet elemental mercury concentrations were typically greater than 0.5 μg/Nm^3 even for fresh, high performing catalyst.

Relative accuracy tests, comparing Hg SCEM results to Ontario Hydro method results, showed mixed results during this project. Oxidation catalyst pilot unit inlet flue gas relative accuracy tests generally showed acceptable agreement between the two methods for both total mercury concentrations and percent oxidation. At the catalyst outlet locations, the total mercury concentrations typically showed good agreement, but the oxidation percentages often did not agree between the two methods. The reasons for these discrepancies remain unclear.

Some possible explanations have been proposed. One is that the Ontario Hydro measurement takes an integrated sample over a two-hour period, while a single SCEM has to alternate between catalyst inlet and outlet, and measuring total and elemental mercury over this same period. Given the observed temporal variations in total mercury and mercury oxidation at some sites, the fact that the two methods measure averages over differing time periods within the two-hour window may explain some of the discrepancies.

However, it is still possible that the oxidation catalyst technology confounds the chemistry involved in one or both methods. For example, the oxidation catalysts could change the oxidation state of other metals in the flue gases, which could impact measurement chemistry in impinger solutions, or the oxidation catalysts could form an Hg^{+2} compound other than mercuric chloride that measures differently. At this point, it is not certain which measurement technology provides a better measure of catalyst performance.

Ultimately, the objective of the technology is to increase removal of mercury in a downstream wet FGD system. The ongoing 41992 project has funded a wet FGD pilot unit that is being coupled with the oxidation catalyst pilot unit to allow measurement of how much mercury is scrubbed downstream of each catalyst. A new project, Cooperative Agreement DE-FC26-06NT42778, will allow such measurements to be made on a 200-MW FGD module operating downstream of a similarly sized gold oxidation catalyst installation, on a plant that fires PRB coal.

Control of Fly Ash Buildup

The results from CCS have shown that if horizontal-gas-flow catalysts are to be used in this process downstream of an ESP, it is imperative to continually clean the catalyst with sonic horn energy. It appears that residual electrostatic charge on the remaining fly ash particles combined with laminar flow through the individual catalyst cells results in fly ash accumulation, even downstream of a very efficient ESP. This was not an issue at Spruce, downstream of a baghouse, but again, the economics do not look good for the technology downstream of a baghouse.

The horns must operate reliably for successful catalyst operation without excessive fly ash buildup. In future installations, close attention should be placed on sonic horn reliability. Reliability measures might include overlapping of horn coverage patterns and redundancy in horn air supply and controls. Frequent monitoring of each horn to ensure it is blowing properly is also recommended.

Catalyst Regeneration

The preliminary economics developed as part of this project show that catalyst regeneration can significantly improve the cost effectiveness of this technology. As mentioned above in this section, the current understanding of the low-temperature mercury oxidation catalyst technology is mostly empirical. It is not certain which species is (are) causing the loss of catalyst activity over time.

It is hoped that a future EPRI-funded investigation of catalyst regeneration using spent catalysts from the ongoing 41992 cooperative agreement will provide more insight. This program is expected to provide two benefits to the understanding of catalyst regeneration. First, by conducting a parametric evaluation of the effects of variables such as regeneration temperature and regeneration duration, it is hoped that an empirical understanding of optimum regeneration conditions will be developed. Second, an adaptation of Method 29 will be employed to capture and analyze the species that desorb during regeneration. It is hoped that a better understanding of what desorbs and how that correlates with regeneration conditions that are most effective will provide a better understanding of what deactivates the catalysts. With such an understanding, it may be possible to enhance catalyst life through control of deactivation, and/or it may be possible to use a theoretically based approach to optimizing catalyst regeneration.

6
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